RESTORATION OF THE THIRD LAW OF THERMODYNAMICS IN A QUANTUM REFRIGERATOR MODEL

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I admit that two times two makes four is an excellent thing, but if we are to give everything its due, two times two makes five is sometimes a very charming thing too.

— Fyodor Dostoyevsky, *Notes from the Underground*

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ABSTRACT

Quantum refrigerators are solid-state devices with huge potential benefits in technology. With no moving parts and of microscopic size, they could easily be integrated in existing technology, such as cellphones and computers, to enhance their performance by reducing the energy wasted as heat. In this master thesis we have studied one such device which appeared to violate the third law of thermodynamics, which states that one can not cool a system to absolute zero in a finite amount of time. The original model considered the systems energy-spectrum to be continuous, but by considering the discrete energy-levels of matter which becomes important at low temperatures we found that the third law is restored. Our results confirm that the third law, although initially formulated as a classical theory, is inherently quantum mechanical.

ACKNOWLEDGEMENTS

The topic of this thesis was first presented to me by Joakim Bergli and Iouri Galperine, who together were my supervisors during my master degree. I am very glad that they suggested this specific topic, since it introduced me to the field of non-equilibrium thermodynamics, a field I find extremely fascinating and intend to do further research in. We have had plenty of fruitful discussions that has been very helpful, both for increasing my knowledge of topics relevant to the thesis and my understanding of physics in general.

My office mates and the other people in the AMCS group also deserves thanks, for providing a friendly and productive atmosphere to work in. Jørgen Rørstad, a good friend and distant colleague in Bergen, assisted me by proofreading the thesis so please contact him if you find any spelling errors.

CONTENTS

1

ENTROPY AND THE LAWS OF THERMODYNAMICS

Since their formal conception the four laws of thermodynamics have become some of the most important concepts in physics. They describe relationships between the fundamental quantities energy, entropy, temperature and heat, which are used to characterize thermodynamic systems. The four laws are very useful to test the validity of new physics. If you propose a new theory in physics and it does not obey the laws of thermodynamics, you can be sure there is a mistake in the new theory or the application of the laws. The problem my thesis is focusing on is an example of a system that apparently breaks one of these fundamental laws. Discovering the error in the description of the system that permits the violation is not trivial, and will be the main goal of this thesis.

The four laws of thermodynamics were precisely formulated during the 19th and 20th century and are associated with the names of great physicists like Carnot, Maxwell, Clausius and Nernst. During the industrial revolution which was happening in this period the scientific community was very interested in increasing the efficiency of steam engines, which were the backbone of the revolution. When man started to put domesticated animals to work in front of ploughs and wheeled wagons 6000 years ago villages saw drastic improvement in crop sizes, and the ability to transport large quantities of produce between villages and fields. It was a great improvement of the standard of living in villages of the time. During the industrial revolution the age-old tradition of muscle power was being replaced and outclassed by the powers steel and fire. Horse and carriage was replaced by coal-powered locomotives, ox and plough by the farm tractor, and steam-powered machines replacing manual labour across all areas of industry.

The constant drive to improve efficiency of steam-machines during this period, was a good motivation for scientists of the day to work on developing the laws of thermodynamics. That heat could be used to perform work was evident. However,

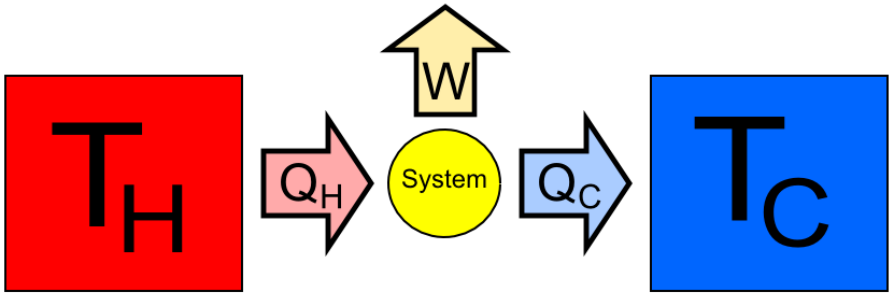

Figure 1: Illustration showing how one can obtain useful work W from the heat flow from a hot to a cold object in an ideal Carnot engine. Here $Q_H > Q_C$ and $W = Q_H - Q_C$.

there were many unanswered questions for the physicists of the day. What is heat in the microscopic scale? What was the highest efficiency you could reach when converting heat-energy to work? What is the connection between heat and mechanical work?

1.1 ENTROPY

> ***You should call it entropy, because nobody knows what entropy really is, so in a debate you will always have the advantage.***
> - John Neumann to Claude Shannon on what to call information (1940) [19].

To understand the laws of thermodynamics it is important to be familiar with the concept of entropy. During the period between his positions as minister of war and minister of interior for Napoleon Bonaparte, the French politician and mathematician Lanzare Carnot published in 1803 his *"Fundamental Principles of Equilibrium and Movement"*, where he stated that in any machine the accelerations and shocks of the moving parts represent losses of moment of activity. His son, Sadi Carnot, continued the work of his father and in 1824 he published a book with the long title of *"Reflections on the Motive Power of Fire and on Machines Fitted to Develop that Power"*. In it he states that whenever a system transfers heat from a hot body to a cold body, one can extract useful work. He realized that this process could be reversed by reinstating the work extracted to produce heat. However the energy content of the heat put into the system would never equal that of the work produced; energy was inevitably lost in the transformation, even for an ideal machine

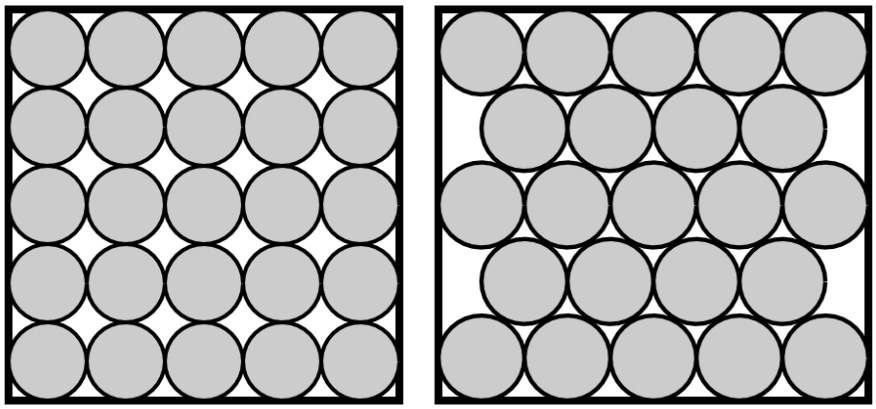

Figure 2: Illustration showing the ambiguity of the order-disorder transformation description of entropy. Which is more disordered, the A-A or the A-B-A layering? Adapted from [2].

with no friction nor imperfections. Moreover he found that the efficiency of the transformation depended only on the temperatures of hot and cold body involved in the process, not on the mechanics of the system itself.

$$\eta_C = \frac{W}{Q_H} = \frac{Q_H - Q_C}{Q_H} = 1 - \frac{Q_C}{Q_H} = 1 - \frac{T_C}{T_H}$$

The Carnot efficiency, η_C, is that of an ideal reversible process, and thus represents an upper boundary on the performance of any real machine. This loss of useful heat energy in a transformation was a precursor for what would be known as the inevitable increase in entropy. It was Rudolf Clausius who gave this property of irreversible heat loss its current name. Entropy is the Greek word for transformation, and he chose it due to the similarity with the word energy.

There is much ambiguity, and even controversy, in the literature when it comes to defining entropy [2]. Usually it is described as a measure of the increase in the disorder, the spread of energy, or the uncertainty of a system. All of these *qualitative* descriptors can useful when one wants to describe what happens in a given system where the entropy increases, yet none of them are *quantitative* definitions of what entropy is.

The most popular and oldest descriptor is the order-disorder interpretation. Disorder is an ambiguous word and one may think that in a disordered system things are not where they should be. The particle components of a "disordered" gas still

obeys Newtonian laws and energy conservation. Can you tell which of the configurations shown in Fig.(2) is more ordered?

1.1.1 *Classical and Statistical Entropy*

There is however no ambiguity in the mathematics that describes entropy. In classical thermodynamics the existence of entropy is postulated by the second law. Building on the work of Carnot on the irreversible loss of usable heat-energy in a transformation, Rudolf Clausius was the first to propose a mathematical theory of entropy [4]. He realized that all spontaneous processes that occur in nature are associated with a definite direction. This is a somewhat obvious fact; if you put milk in your coffee the molecules of the milk mixes with the molecules of the coffee and result an homogeneous mixture, but this mixture never spontaneously separate back into two phases again. And if this coffee was hotter than its surrounding, heat always flows out of the coffee and into the environment until the temperature of the cup of coffee is equal to that of its environment. Once this temperature equilibrium is obtained, heat is never spontaneously transferred back into the coffee, increasing its temperature. Clausius defined a new quantity he called the equivalence value, which is what we now refer to as temperature. When a small quantity of heat is introduced into a system at a temperature T, he defined the change in entropy as

$$dS = \frac{dQ}{T}$$

Whenever we move from one equilibrium state to another by varying some parameter of the system or removing some constraint the entropy always increases, unless the transformation is ideal and reversible which results in no change in the entropy.

At the time of Clausius, Maxwell and Carnot, the microscopic properties of gasses, liquids and solids were not understood. Nobody knew about the atom, and heat was considered a form of liquid which they called "caloric". However, to precisely define entropy we need a complete description of the microscopic state of systems. The Austrian Ludwig Boltzmann is considered the father of statistical mechanics, which is the scientific theory that is used to describe the macroscopic properties of a system by considering its microscopic constituents. In his times, the physics establishment did not believe in the atomic

and molecular theory. They considered it a convenient theoretical construct, not a fact of nature. In his "*Kinetic Theory of Gasses*" Boltzmann considered a gas made up of N molecules, bouncing around in a volume V. The total internal energy of this gas is equal to the sum of the kinetic energies of all its constituent molecules. The microstate of a system is a complete and exact description of all its constituents, thus in the case of an ideal gas it is the position and velocity of every molecule.

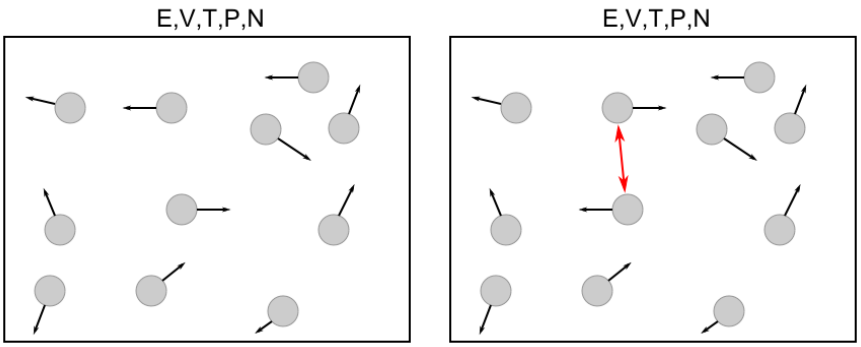

Figure 3: Illustration of an ideal gas composed of N molecules, in a volume V, with pressure P, temperature T and energy E. By exchanging the position of the two molecules shown we create a new microstate, but the macrostate of the system remains the same.

Boltzmann realized that there were several ways to create microstates with the exact same pressure, energy and volume, or in other words, with the exact same macrostate. There is no change in the macroscopic state of the ideal gas when you for example saw around the position of two molecules (see Fig.(3)). It is clear that for the ideal gas there is a large number (far larger than the number of molecules) of microstates that gives the same macrostate. Boltzmann postulated a relationship between the entropy of a system and the total number of microstates that is characterized by its macroscopic state.

$$S = k_B \log W \tag{1}$$

Here k_B is the Boltzmann constant, and W is the total number of microstates. This formula was a radical new interpretation of entropy, and a first intuition into the probabilistic behaviour of nature. The simple statistical mechanics definition of entropy is that the more microstates there are that result in the same macrostate, the more likely it is for the system to be in that

state, and we say that the entropy is then maximized. Thus entropy can be considered a measurement of the number of microstates a system can attain for a given macrostate.

1.1.2 *Aspects of Entropy*

The description of the microstate of most real systems is generally more complicated than that of the ideal gas. For the ideal gas the internal energy of the system consist entirely of sum of the translational energy of all its molecules. We can complicate the situation by considering an ideal diatomic gas, where energy can also be stored in the rotation of each molecule. Now the internal energy of the gas is given by the sum of the translational and rotational energy of all the constituent molecules. These different ways of storing energy in a system is traditionally called degrees of freedom. It should be clear that when you have more ways of storing energy in a system, you also have more microstates that corresponds to the same macrostate. The number of "equal" microstates of the diatomic gas increases relative to that of the ideal gas by the number of permutations of the rotational energies each molecule can attain that returns the same total energy.

Entropy is not only associated with the degrees of freedom of a system. Take the entropy of mixing for example; when you mix two miscible fluids made up of molecule A and B, there is an increase in entropy. This increase in entropy does not occur when you mix two identical fluids. The total entropy of a system has to be considered a sum of the entropy of all its parts, and we call these different parts the aspects of entropy in the system. Entropy can flow between these aspects without changing the total entropy of the system. This property is utilized in nuclear demagnetization. The entropy of a crystal is associated with two aspects: the spin, and the vibrational motion of its atoms. By isothermally aligning the spin of a crystal with a magnetic field (thus decreasing the entropy of the spin aspect), and then thermally insulating the crystal, entropy will flow from the vibrational aspect into the spin aspect of the crystal.

1.2 THE 0TH LAW

> ***All heat is of the same kind.***
> - Maxwell, J.C. (1871) [23].

The zeroth law is the first of the four laws, and is easily understood through common sense. Assume you have three systems, lets call them A, B, and C, which are all in thermal contact with each other as shown in Fig 1. This means that they can all exchange heat freely across the system borders. If you are told that B is in thermal equilibrium with both A and C, you can be certain that A and C is in equilibrium with each other as well.

This law allows for a definition of the property know as temperature. All the internal energy which passes from A to B is balanced by an equal exchange from B to A when the systems are in thermal equilibrium. This is true even if the microscopic properties like the specific heat or the mass of the particles of the systems differ. Thus it is implied that there is another measurable quantity which heat transfer depends on that is the same for the two systems. This property is called the temperature of the system.

1.3 THE 1ST LAW

> ***In all cases in which work is produced by the agency of heat, a quantity of heat is consumed which is proportional to the work done; and conversely, by the expenditure of an equal quantity of work an equal quantity of heat is produced.***
> - Clausius, R. (1850).

The first law of thermodynamics is also one of the less esoteric of the four laws. It is essentially the thermodynamic formulation of conservation of energy. Any change in the internal energy of a system is associated with transfer of heat between the system and its environment and/or an amount of work done by or on the system. The change in internal energy of a system is equal to the difference between the heat added to a system, and the work performed by the system. Mathematically this law can be expressed through the fundamental thermodynamic relation, which is shown below.

$$\Delta U = Q + W \tag{2}$$

Here U is energy, Q is heat, and W is work. Any change of energy in a system can be attributed to either an addition or removal of heat energy, or an amount of work performed on or by the system. By convention work is considered negative if it is performed by the system as it uses up some of its free energy in the process. With this sign convention consider the work performed in an expansion of a gas

$$W = -PdV$$

where P is the pressure of the gas and dV the change in volume. If the gas is allowed to freely expand dV is positive and W negative, thus the gas performs work and reduces its internal energy as long as no heat is added in the process. If the gas is compressed by some outside force dV is negative and W positive, increasing the energy U of the system, again assuming no heat is exchanged with the environment. The first law connects the concept of internal energy with measurable quantities like temperature and pressure, and shows that its natural variables are entropy and volume. This equation can in combination with other thermodynamic potentials (Gibbs and Helmholtz free energy, Enthalpy, etc.) be used to derive the Maxwell relations, an important set of differential equations in thermodynamics.

1.4 THE 2ND LAW

> ***Every process occurring in nature proceeds in the sense in which the sum of the entropies of all bodies taking part in the process is increased. In the limit, i.e. for reversible processes, the sum of the entropies remains unchanged.***
> - Planck, M. (1926).

It is said that the second law of thermodynamics has as many formulations as there are scientists who study it. This is probably because the second law is not as intuitive as the preceding laws. In simple words the law states that any addition of heat to a system is accompanied by an increase in the total entropy of the system. If the process that adds heat is reversible the entropy will remain the same, but in no way can you ever have a process which adds heat while reducing the entropy. The second law can be formulated mathematically through Clausius inequality which is given in Eq.(3).

$$\Delta S = \oint \frac{\delta Q}{T} \geqslant 0 \tag{3}$$

The equality holds only for reversible processes, where the net change of entropy is zero. Naturally it is possible to decrease the entropy by performing work on the system, but the entropy may never spontaneously decrease. The second law states that for large systems and time scales that average out small fluctuations, the entropy production is inevitably positive.

2

THE THIRD LAW

> ***The entropy change in a chemical reaction tends to vanish as the temperature approaches absolute zero.***
> - Nernst, W. (1906)

Since the third law of thermodynamics is the one most relevant to the topic of this master thesis, it deserves a chapter of its own. Later I will formulate the thesis model in detail, but for now I will say that the third law is apparently violated in the system of interest, and the main objective is to find out exactly how it happens and propose a solution to the inconsistencies. The third law of thermodynamics has its origin in the heat theorem put forth by Walther Nernst in 1906 [24], which is given in the quote at the beginning of this chapter. Nernst proposed the law in order to predict the equilibrium conditions of chemical reactions, but it soon became clear that there was something profoundly fundamental about his statement.

Following the publication by Nernst, a discussion followed between him and two other notable physicists: Max Planck and Albert Einstein. They argued about the implications and interpretations of the heat theorem, and now 100 years after this discussion we still have multiple statements of the third law which are not trivially equivalent.

• **Nernst-Simon statement:** The entropy change associated with any reversible isothermal process in a system at absolute zero tends to zero [30].

$$S(T, x) - S(T, x + \delta x) \to 0 \qquad \text{as } T \to 0K$$

• **Planck statement:** The entropy of a perfect crystal is exactly zero at absolute zero temperature [28].

$$S(T, x) \to 0 \qquad \text{as } T \to 0K$$

• **Einstein statement:** The entropy of any substance tends to a constant value as the temperature falls to absolute zero [8].

$$S(T, x) \to S_0 \qquad \text{as } T \to 0K$$

In all these definitions, x represents some parameter of the system (e.g. pressure, volume, magnetic field). Although these statements may seem similar, the strength of their claims vary. The Planck formulation specifies the entropy of a perfect crystal, which has a non-degenerate unique ground state at $T = 0K$. By setting $W = 1$ in the Boltzmann formula in Eq.(1), we see that this corresponds to an entropy $S = 0$. Einstein pointed out that some system has degenerate ground-states, such that $W > 1$ at absolute zero and thus $S > 0$. Thus there are two general requirements for the entropy of a system to go to zero at absolute zero: the energy levels of the system has to be quantized, and its ground state must be non-degenerate.

Classical thermodynamic as it is derived from the first and second law forms a closed and completed subject [34]. This is because the concept of entropy as defined by the second law in classical thermodynamics can be used for predictions, regardless of our knowledge of the microscopic or statistical details of the system under investigation. However a complete analysis of a system via the third law is only possible when considering entropy as a statistical quantum mechanical concept, like Einstein suggested.

2.1 CONSEQUENCES OF THE THIRD LAW

Consider for simplicity the Planck formulation of the third law, which applies for crystal systems. One of the most important consequences of the third law, is that the specific heat tends to zero at absolute zero. This can be shown for specific heat at constant pressure by considering the following equation.

$$C_p = \left(\frac{dQ}{dT}\right)_p = T\left(\frac{\partial S}{\partial T}\right)_p = \left(\frac{\partial S}{\partial \ln T}\right)_p \tag{4}$$

As T approaches zero, ln T tends to minus infinity and S to zero. Thus we obtain $C_p \to 0$, and similar proofs exist for the other specific heats. The vanishing of the heat capacity allows us to use absolute zero as a reference for all thermodynamical calculations. We can see this by using the second law, Eq.(3), which originally only treats entropy differences.

$$S_T - S_0 = \int_0^T \frac{C_V dT}{T} \tag{5}$$

The third law tells us that $S_0 = 0$, and we are able to assign a unique value, S_T, of the entropy to a system at any temperature.

$$S_T = \int_0^T \frac{C_V dT}{T} \tag{6}$$

Most systems reach approximately zero entropy before $T = 0$ K, but it is important to realize that the third law only claims validity at the very limit of $T \to 0$ K.

From Maxwell's thermodynamic relations we can understand many properties of a thermodynamic system via the third law. One of the relations is given by

$$(\frac{\partial V}{\partial T})_p = -(\frac{\partial S}{\partial p})_T \tag{7}$$

and since the third law predicts that the entropy difference ∂S vanish as $T \to 0$ we obtain

$$\lim_{T\to 0} (\frac{\partial V}{\partial T})_p = 0 \tag{8}$$

which tells us that the expansion coefficients of a system goes to zero as the temperature approaches zero. Thus at very low temperatures the volume of a system changes little as a function of temperature. For magnetic materials the Maxwell relation gives us

$$(\frac{\partial M}{\partial T})_H = (\frac{\partial S}{\partial H})_T \tag{9}$$

where M is the magnetic moment, and H the applied field. The magnetic moment and field are related by $M = \chi H$, where χ is the magnetic susceptibility.

$$\lim_{T\to 0} (\frac{\partial \chi}{\partial T})_H = 0 \tag{10}$$

Therefore, in the limit of $T \to 0$ susceptibility of all magnetic materials must be independent of temperature. Magnetism can arise from various different mechanisms; nuclear spin, electron currents, dipole moment, etc. Nevertheless as these can be considered different aspects of a system that carries entropy, the third law guarantees that the susceptibility goes to zero at zero temperature for all of them individually.

2.2 HELIUM AND THE THIRD LAW

An apparent contradiction to the third law is found in the absence of solidification in helium. Usually found in gas form, helium liquefies at about 4 K. As the temperature is decreased further helium stays liquid even at the lowest temperatures we can produce today. Very high pressure is required to solidify helium, which begs the question; since solids are associated with lower entropy than liquids, is helium in contradiction of the third law? Quite contrary we will see that helium provides potent evidence for validity of the third law. Heisenberg's uncertainty principle tells us that we can never precisely determine both the position and momentum of a particle simultaneously. This is not due to our experimental inability to perform the measurement, but rather a fundamental fact of nature.

$$\sigma_x \sigma_p \geqslant \frac{\hbar}{2} \tag{11}$$

Here σ_x and σ_p is the uncertainty in position and momentum respectively. Each atom in a crystallized solid is localized to within the atomic spacing parameter, a, thus the momentum of the atoms have an uncertainty on the order of $\hbar/a$ which results in a contribution to the kinetic energy of the order $\hbar^2/ma^2$. Since this energy is inversely proportional to the square of the atomic spacing it results in an internal pressure which tends to increase the volume of the crystal. In most condensed systems the repulsive zero-point energy is negligible when compared to the other attractive binding forces present, however helium is one of the few exceptions. It is a closed shell element where the only binding forces are the van der Waal's forces, and even they are very small. In fact the van der Waal's forces are so small that they are comparable to the zero-point energy. The internal pressure of helium due to the repulsive zero-point energy counteracts any tendency to crystallize due to the binding forces. The Clausius-Clapeyron relation can be used to characterize discontinuous phase transitions, and is given by

$$\frac{dp}{dT} = \frac{\Delta S}{\Delta V}$$

where ΔS and ΔV are the change in entropy and volume during the transition from one phase to another. Measurements show that for helium dp/dT vanishes, while ΔV tends to a constant value, for helium at low temperatures [34]. This implies that the entropy difference between the two phases ΔS also tends

to zero at absolute zero, in accordance with the third law. The vanishing entropy difference between liquid and solid helium also tells us that there is no latent heat of melting, and that the liquid helium is in a highly ordered state, comparable to that of a solid. In fact, below the so-called lambda point (2.17 K), helium experience a phase-transition and becomes a superfluid. The superfluid helium (usually called He-II where He-I is the normal fluid), is analogous to a Bose-Einstein condensation and behaves as a fluid with zero viscosity and zero entropy.

Helium comes in two basic isotopes, ^4He and ^3He. Their behaviour is mostly identical, the main differences being that ^3He has a lower mass and also a net nuclear spin. The lower mass means that its zero-point energy is larger, hence its vapour pressure is higher than that of ^4He. In a mixture at temperatures above $\sim 1K$, ^4He and ^3He are completely miscible, which results in a high mixing-entropy. We can also find a Maxwell relation for surface energy by including the surface energy, γA, of a system.

$$(\frac{\partial \gamma}{\partial T})_A = (\frac{\partial S}{\partial A})_T \tag{12}$$

Here σ is the surface tension and A the area. By applying the third law we obtain

$$\lim_{T \to 0} (\frac{\partial \sigma}{\partial T})_A = 0 \tag{13}$$

The third law states that the entropy of mixing must vanish as the temperature tends to zero. When the mixture reaches a temperature of $\sim 1K$ a phase separation of the two isotopes occur, where ^3He separates from ^4He due to its higher zero-point energy. As the temperature approaches zero this phase separation results in two phases of pure ^3He and pure ^4He, so that the entropy of mixing reaches zero. The third law says nothing about *how* the entropy of a system vanish at zero kelvin, it only states that it *must*. It so happens that in this system a phase separation satisfies the demands of the third law.

2.3 NON-EQUILIBRIUM DEGREES OF FREEDOM

In section 1.1 we discussed how each aspect/degree of freedom of a system has an entropy associated with it. For the third law to be valid the system has to be in internal equilibrium,

i.e. it can not be in the process of undergoing a transformation. When one tries to apply the third law for a system with aspects that are out of equilibrium, one finds a non-zero entropy at absolute zero. In this section we will discuss the entropy of metastable states and glassy systems to illustrate this behavior. Glass systems are amorphous solids that are characterized by an absence of the long-range we find in crystals.

It is possible for some substances to remain in its liquid form, even when temperature is lowered below the freezing temperature. A liquid in this form is said to be *supercooled*. It typically happens for pure liquids that lacks a nucleation point, or seed crystal. Lacking any such nuclei, the liquid can be cooled below the freezing temperature temperature before any crystallization occur and it will become an amorphous solid.

The specific heat as a function of temperature for such a liquid is shown in Fig.(4). The substance can exist in three different phases; a crystal phase (a), a supercooled liquid phase (b), and a glass phase (c). In its crystalline form the specific heat is a result of the vibration of its atoms about their mean position in the crystal lattice. The specific heat of a liquid (supercooled or not) is far greater than that of a crystal due to the complex types of motions possible for a system of unbound atoms. However as the supercooled liquid approaches T_G its atoms slows down considerably and the range of motion is limited. In the glass phase (c) the atoms cannot change their configuration in any reasonable time, and its specific heat is characterized by vibrational motions in common with a crystal.

The entropy difference between the glass and crystal phase is given as a function of temperature in Fig.(5). The value of this difference corresponds to the configurational entropy of the glass which is frozen-in after the transition from supercooled liquid to glass. This entropy increases with the complexity of the molecular motion of the molecules that was frozen. The non-zero entropy at absolute zero seems to be a violation of the third law of thermodynamics, however this is not the case.

Consider the illustration shown in Fig.(6). It shows three different potential landscapes.

(**a**) shows a well defined stable equilibrium where the system (the black dot) lies in the global minimum of the potential, and attains the lowest possible energy.

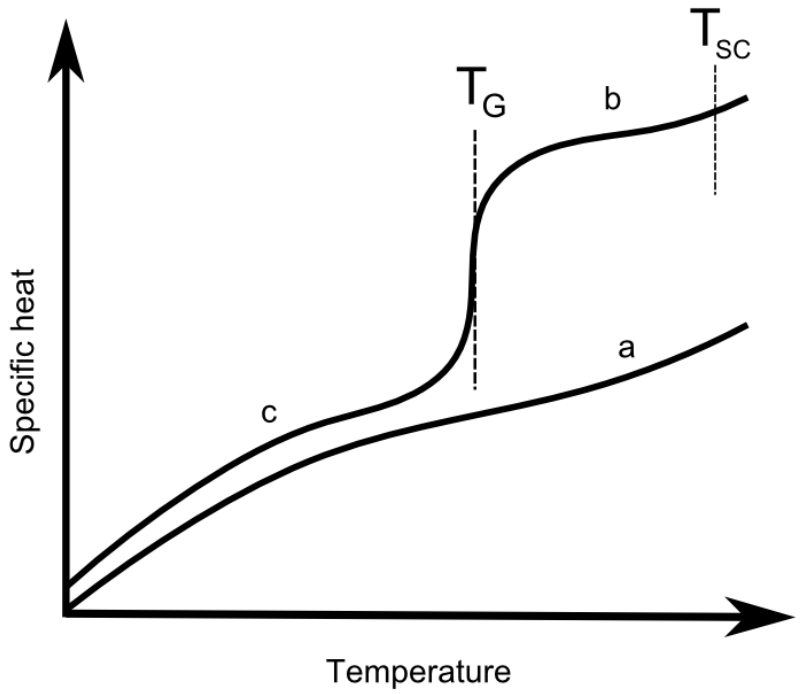

Figure 4: The specific heat versus temperature for a glassy system. The substance can be in crystal phase (a), a supercooled liquid phase (b), or a glass phase (c). At T_{SC} the liquid should crystallize, but the lack of a nucleation point leads to a supercooled state. If this supercooled state remains until the glass transition temperature T_G is reached, the liquid becomes a glass with "frozen-in" disorder.

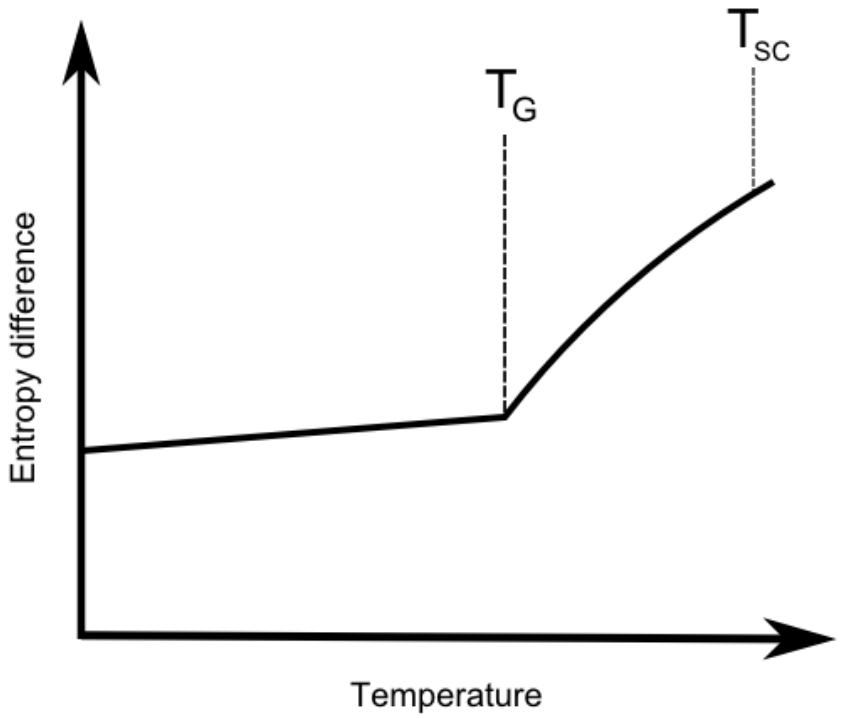

Figure 5: The entropy difference between the crystal and glass state, as a function of temperature. While the liquid exists in a supercooled state its entropy slowly approaches that of the crystal, but if the liquid does not crystallize before the glass transition temperature T_G it will become an amorphous solid. The "frozen-in" disorder of a glassy system results in a non-zero entropy even at $T = 0$ K.

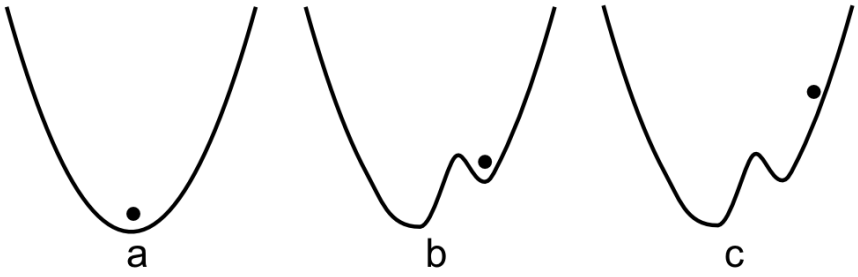

Figure 6: Illustration of the potential energy landscape for a stable equilibrium (a), a metastable equilibrium (b) and a non-equilibrium state (e.g. a glass system) not describable by classical thermodynamics (c).

(**b**) is a metastable state where the system is in a local minimum of the potential, but does not have enough energy to overcome the adjacent potential barrier to reach the global minimum. As long as the perturbation is small enough a system displaced from its local valley tends to return to its local minimum, and thus the system has well defined properties describable by thermodynamics.

(**c**) represents a state which is not describable by classical thermodynamics. The system is slowly moving towards a local or global equilibrium, but the viscosity is so high that the relaxation time is close to infinity (relative to the relevant time-scales of the system) and the system is "stuck" at the potential wall.

A glassy system is an example of the potential situation shown in (c), where the molecules of the glass can not take up their positions of least energy, and is not considered a thermodynamically well-defined state. The excess entropy of glassy systems disappears if we let the system rest between each successive temperature reductions, i.e. if we cool the system slowly. Thus the thermodynamic properties of such a system depends on its history; rapid cooling across the glass transition temperature freezes in more disorder than a slow cooling.

The third law requires thermodynamic equilibrium of the different aspects of a system, and this is a general restriction inherent in all the laws of thermodynamics [34]. The first and second laws are statements of thermodynamic state functions (energy, pressure, volume, etc.) which are only defined in equilibrium conditions in classical thermodynamics.

2.4 THE UNATTAINABILITY OF ABSOLUTE ZERO

It was also Walther Nernst that first realized an important implication of the third law of thermodynamics; it is impossible to cool any system to absolute zero in a finite amount of time [25]. The reasoning behind this realization is easily explained by considering Fig.(7), Fig.(8), and Fig.(9). First in Fig.(7) we show a generic entropy diagram which can be used to produce cooling. Assume that the entropy is dependent on some other variable than temperature (in the digram we use x_1 and x_2 to be as general as possible), for example pressure or volume. A recipe for the cooling of this system is then given by the following:

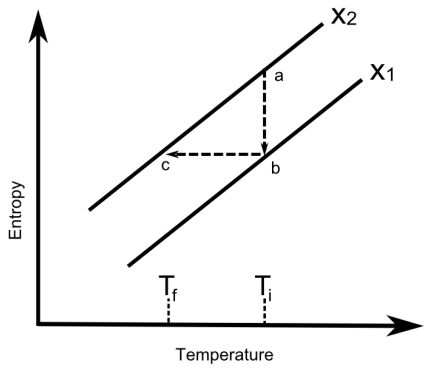

Figure 7: Diagram of entropy versus temperature, where the entropy is dependent on some parameter other than temperature (a generic variable x). The system can be cooled from T_i to T_f by following the process (a)→(b)→(c).

1. The procedure starts at (a) with temperature T_i on the entropy curve of the parameter $x = x_2$ such that $S\big(x_2(T_i)\big) > S\big(x_1(T_i)\big)$.

2. By varying the parameter x isothermally from x_2 to x_1 the entropy is reduced along the path (a)→(b) by removing an amount of heat equal to $T_i \Delta S$.

3. Isolating the system and restoring the parameter x adiabatically to its original value $x = x_2$ along the isentropic path (b)→(c) returns the maximum cooling and the temperature falls from T_i to T_f.

4. The procedure can now begin anew from step 1.

Consider the Nernst-Simon statement of the third law of thermodynamics; the entropy differences associated with a system approaches zero as the temperature tends to zero. In Fig.(8) the entropy diagram of a system that does not obey the third law is shown. For this system the cooling process (a)→(b)→(c) can lead to a temperature of absolute zero. However the entropy diagram of any real system will look like the one in Fig.(9), where the entropy difference tends to zero at zero kelvin. Since the entropy curves of x_1 and x_2 comes together at $T = 0$ K, the process (a)→(b)→(c) can never lead to absolute zero in a finite amount of steps.

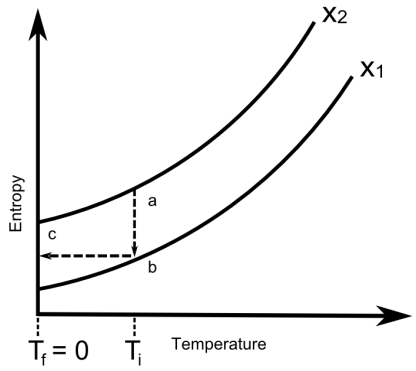

Figure 8: Here the entropy difference is non-zero when varying the parameter x between $x = x_2$ and $x = x_1$. The result is that the process (a)→(b)→(c) can be performed to reach absolute zero in a finite amount of time.

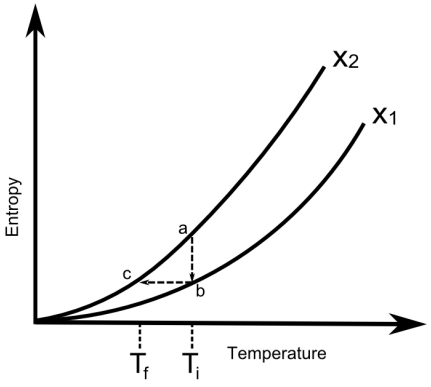

Figure 9: A system with zero entropy difference at $T = 0$ K, as shown in this figure, obeys the third law of thermodynamics and will never attain absolute zero in a finite amount of time.

We mentioned earlier that glassy systems has large non-zero entropy difference that may persist down to absolute zero, but this entropy difference can not be used to attain low temperatures as the molecules of the glass are frozen-in and can not be varied by any external parameter [34]. To put mathematical weight behind these illustrations, consider the following process; a system is varied adiabatically from a state with temperature T_i and an associated entropy S_1^b, to another state with lower temperature T_f and entropy S_2^c. This is the process $b \to c$ as indicated in the figures. This adiabatic process driven by varying an entropy-dependent parameter from X_1 to X_2. Since no heat is exchanged in an adiabatic process we have in general

$$S_2^c \geqslant S_1^b \tag{14}$$

where a reversible process is represented by the equality sign. Applying the second law we obtain

$$\int_0^{T_f} \frac{C_c}{T} dT \geqslant \int_0^{T_i} \frac{C_b}{T} dT \tag{15}$$

If we want to cool to absolute zero ($T_f = 0$) we obtain $S_2^c = 0$, and thus

$$\int_0^{T_i} \frac{C_b}{T} dT \leqslant 0 \tag{16}$$

With the exception a few notable exotic examples (i.e. black holes, neutron stars [18]), the specific heat is always a positive quantity; when you add heat to a system its temperature increases. For Eq.(16) to be true C_α has to be a negative quantity, and we conclude that the end temperature T_2 can not be absolute zero.

To conclude this chapter, here is a word of encouragement to all those who feel that the unattainability of absolute zero temperature is a road block for the advancement of science and our understanding of the universe. Although the third law forbids us to ever reach absolute zero, there is no need to despair. We can get as arbitrarily close as we want, or need, to make measurements of any quantities of thermodynamic interest.

3

VIOLATIONS OF THE LAWS OF THERMODYNAMICS

Throughout scientific history scientists and laymen alike have (to the best of their respective abilities) tried to challenge, bend, and break the fundamental laws of thermodynamics. They are one of the greatest pillars which carries the weight of the modern science, and as there is a part in the human psyche that enjoy watching great structures fall to the ground, there are no better targets for destruction than the laws of thermodynamics. In this section I will introduce some of the ways the laws have been challenged, from perpetual motion machines in the early middle ages even before the laws were formulated, to cutting edge modern science like the recent problem of degeneracy in the zero kelvin ground state in spin-ice. The one thing all the cases discussed have in common is that the violations are *always* illusions, and the pillars of thermodynamics remain strong.

3.1 THE SECOND LAW

This is probably the most challenged, yet most robust law there is in physics. A consequence of the second law is that there can not exist a perpetual motion machine. A perpetual motion machine is a general term for something that operates without dissipating energy, which results in an efficiency of 100%. Needless to say, it would be a very useful machine, and throughout history inventive people have imagined and built contraptions which they have claimed to be perpetual motion machines. One of the first was the "magic wheel", invented in Bavaria in the 8th century [7]. It consists of a wheel rotating on a well lubricated axis with a series of counterweights. Friction naturally slows down and eventually stops the wheel, but the rotation time was reportedly very long.

Perpetual motion is a long lost dream today, only occupying the minds of charlatans and crackpots. There is however other aspects of the second law that is still a point of controversy for physicists today. Most believe that the second law has never been violated, and never will be, but others claim to find exper-

imental violations. Maxwell stated in 1878:

> ***The truth of the second law is therefore a statistical, not a mathematical, truth, for it depends on the fact that the bodies we deal with consist of millions of molecules, and that we never can get a hold of single molecule.***
> - J.C. Maxwell (1878) [22]

History have shown his argument false however, since we now have single particle thermodynamics well formulated in quantum statistical mechanics. He was also a highly religious evangelical who believed in the literal interpretation of the bible and did not at all like the random nature of thermodynamics. He felt that the second law was not an universal law of nature, but rather a result of flawed human perception and lack of information, and he introduced the famous Maxwell's Demon as an argument against the second law [14].

3.1.1 *Fluctuations*

Even though the second law says that the entropy of a closed system always increases, and that heat-energy always flows from hot regions to cold regions, there will always be statistical fluctuations that can momentarily result in a decrease in entropy. Imagine a small machine, where the work performed over a cycle is comparable to the thermal energy $k_B T$ of the environment at temperature T. In this situation the machine is expected to be able to operate in reverse, i.e. the surrounding heat energy can be converted into useful work and allow the machine to run backwards over short time-scales. In macroscopic systems this is a strong violation of the second law of thermodynamics, where entropy is reduced/consumed rather than produced.

A quantitative explanation on the boundaries of violations of the second law in finite systems was given in 1993 Evans et al. with the introduction of the fluctuation theorem [11]. It is a mathematical expression for the probability that heat-flux flows in the opposite direction of the flow dictated by the second law. Or in other words, a theorem that can predict when entropy consumption violate the second law for small systems and time scales. The fluctuation theorem relates the probability

of observing a phase-space trajectory over time τ with entropy production rate $\Sigma_\tau = A$ (where A is positive) to the probability of observing the reverse trajectory with the entropy consumption rate, $\Sigma_\tau = -A$.

$$\frac{P(\Sigma_\tau = A)}{P(\Sigma_\tau = -A)} = e^{A\tau} \geqslant 1 \tag{17}$$

The right side of the equation is always positive and larger than 1, thus the probability of entropy production is always higher than the probability of entropy consumption. Since entropy production is an extensive quantity, meaning it grows with the size of the system, the fluctuation theorem also shows that as the system size grows, the entropy-consuming trajectories becomes less probable and the second law in its macroscopic formulation is recovered.

A recent discussion about the validity of second law comes from a paper published by Wang, G. M et al. in 2002 with the title *"Experimental Demonstration of Violations of the Second Law of Thermodynamics for Small Systems and Short Time Scales"* [32]. In the experiment they follow the trajectory of an optically-trapped bead that is moved around in a water-bath. For each trajectory they calculate the entropy production over the its duration and determine the fraction of trajectories that defy the second-law. They observe entropy consumption (*i.e. negative entropy production*) over colloidal length and time scales which they claim is in direct conflict with the second law. However, in their analysis they neglect to take into consideration the key point of the second law and the fluctuation theorem; the entropy production averaged over time is what matters [26]. No formulation of the second law makes any claims that the unaveraged entropy production has to be positive.

The majority of physicist today agree that there is no violation of the second law when averaged over time. Most of the discussion comes down to defining the boundary between a real violation and fluctuations often observed in experiments. The following quote by Russian physicist Ivan Bazarov captures the general consensus among modern thermodynamicist.

> ***The second law of thermodynamics is, without a doubt, one of the most perfect laws in physics. Any reproducible violation of it, however small, would***

bring the discoverer great riches as well as a trip to Stockholm. The worlds energy problems would be solved at one stroke. It is not possible to find any other law (except, perhaps, for super selection rules such as charge conservation) for which a proposed violation would bring more scepticism than this one. Not even Maxwells laws of electricity or Newtons law of gravitation are so sacrosanct, for each has measurable corrections coming from quantum effects or general relativity.
- Ivan Bazarov (1964).

3.2 THE THIRD LAW

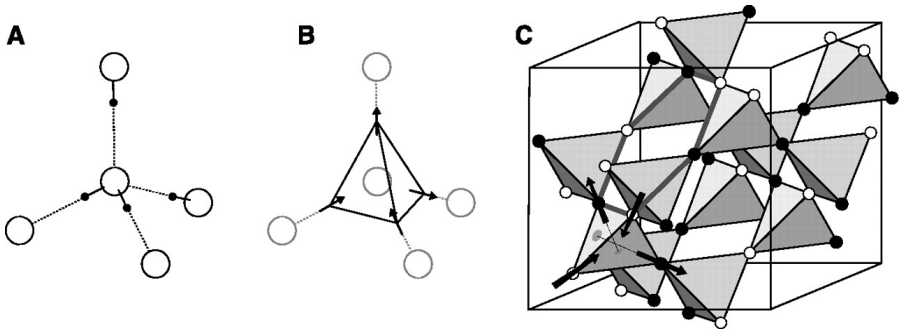

Figure 10: Schematic showing the crystal structure of ice. (A) shows oxygen atoms as white circles and hydrogen atoms, which can either be in a "near" or "far" state, as black dots. In (B) the hydrogen atoms have been replaced by vectors pointing inwards to or outwards from the central oxygen atom, and (C) shows the full crystal structure. From [3].

The third law of thermodynamics, in the Planck formulation, implies that a crystal at absolute zero has to be in a non-degenerate ground state. According to Boltzmann's famous law for entropy, $S = k \ln W$, if $S = 0$ then the number of available microstates of a system has to be $W = 1$. Thus at $T = 0$ only a single non-degenerate ground state can exist.

It was noted in 1935 by Linus Pauling that water ice, due to its structure, was expected to have non-zero entropy even when cooled down to absolute zero temperature. Water ice contains oxygen atoms tetrahedrally coordinated with four other oxygen atoms, as shown in Fig.(10A). The large white circles represents the oxygen atoms, and the small black circles are hydro-

gen atoms. Each oxygen atom have four neighboring hydrogen atoms, where two are near covalently bonded (forming the familiar H_2O molecule) and the other two are far and hydrogen bonded to the oxygen [3]. Naturally the hydrogen atom that is "far" with respect to one oxygen atom, is "near" to another. In Fig.(10B) the position of the hydrogen atoms have been replaced with displacement vectors, with directions inwards and outwards, placed at the midpoints between two oxygen atoms.

Pauling realized that the nearest-neighbor interactions results in the same energy contribution if two of the vectors are outgoing and two are incoming. There are 6 different ways to arrange the four vectors into two incoming and two outgoing ones, thus the ground state of the molecule is not unique. In Fig.(10) the lattice of an ice crystal is shown. For clarity the black dots represents a spin pointing into a downward tetrahedron while the white dots represent the opposite, resulting in two black dots and two white dots per tetrahedron. Each tetrahedron have approximately entropy of $k_B \ln(6)$ associated with it. Since the tetrahedrons are not independent of their neighbors, the real entropy is a bit less, but the results are the same; the entropy of the system scales with the number of tetrahedrons, i.e. the size of the system. This volume-extensive entropy seems to violate the third law of thermodynamics.

When considering the third law it is important to follow its instructions precisely as defined. One has to take the true limit of $T \to 0$ K. That is, if the system you are observing has a degenerate ground state at low temperature, you can not claim that the third law is broken. You have to further reduce the temperature to reach the limit imposed by the third law, which undoubtedly will appear. In the case of spin-ice, which is the spin analogy of the structure in Fig.(10), it has been recently shown in 2014 that the next-nearest neighbour interaction play an important part to lift the degeneracy of the low temperature ground state [15]. The authors fabricated a thin sheet of a material with similar properties as spin-ice, to enhance the importance of higher order interactions than the nearest-neighbor ones. They found that for temperatures higher than 2 K the distinct spin-ice characteristics were observed in the films, but at lower temperatures evidence of a zero entropy state was found. When taking into consideration the higher order interactions in the thin films the earlier statement that all the tetrahedrons carry the same

amount of energy breaks down. These very weak interactions introduce new terms to the Hamiltonian of the system, and results in tiny energy differences between the previously "degenerate" ground-states. Regardless of the magnitude of the energy differences of the lower states, at low enough temperature the ground state will be uniquely defined. And the third law only claims validity at precisely these infinitely small temperatures.

4

THE BOSON DRIVEN REFRIGERATOR

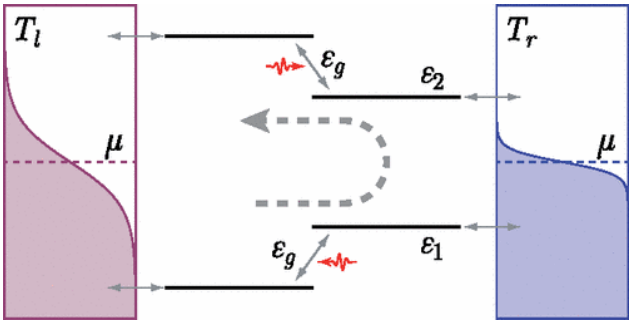

Figure 11: Schematic of the refrigerator. The left side is a hot lead with temperature T_L and chemical potential μ, while right side is a cold lead with temperature T_R and chemical potential μ. The two leads are connected by two quantum dots, which allows for particle transport between the two reservoirs. Illustration from [5].

Here we will introduce the main topic of the thesis; a refrigerator system that absorbs hot photons from the Sun to induce cooling in one of its reservoirs. We will not go into the mathematical details of the model here. In this chapter we introduce the model qualitatively, and save the quantitative analysis for Chapter 6. We will learn that the model violates one of the formulations of the third law, the unattainability principle, and we will discuss the comments made on the published article to get an overview of the response of the scientific community.

4.1 INTRODUCTION OF THE REFRIGERATOR MODEL

According to the second law, heat energy always flow from regions of high temperature to low temperature until both regions reach the equilibrium temperature and no further heat is exchanged. In a paper by B. Cleuren et al.[5] a new mechanism for refrigeration powered by photons have been proposed. Two metallic leads are connected by two quantum dots as shown in Fig.(11). The cold right lead has the temperature T_R, while the hot left lead has temperature T_L. Since $T_L > T_R$ the Fermi-distribution of the left lead has a longer tail as indicated in the

figure. Each quantum dot acts like an atom that can accept a single electron in one of two energy levels. The quantum dot closest to the right lead contains the energy levels ϵ_1 and ϵ_2, while the one closest to the left lead contains the other two levels denoted $\epsilon_1 - \epsilon_g$ and $\epsilon_2 + \epsilon_g$. With an arrangement of the quantum dot energy levels as shown in Fig.(11), two channels for the electron-transfer between the metallic leads are formed. One via the "lower" energy levels, ϵ_1 and $\epsilon_1 - \epsilon_g$, and the other via the "upper" energy levels, ϵ_2 and $\epsilon_2 + \epsilon_g$.

By adjusting the energy-levels of the two quantum dots one can induce a flow of hot electrons from the cold lead to the hot lead (via the upper channel above the chemical potential), and a flow of cold electrons from the hot lead to the cold lead (via the lower channel below the chemical potential). The particle current will then flow in the direction indicated by the gray arrow in Fig.(11). The net result is a cooling of the right lead, and a heating of the left one. The electrons are effectively evaporating out of the cold lead and condensing into the hot lead. Transport between the energy levels of the quantum dots is mediated by hot solar photons, thus the proposed nano-machine can be considered as a mechanism for cooling by heating.

The authors assume the two levels of each channel can not be simultaneously occupied, i.e. there can not be an electron in both the levels ϵ_1 and $\epsilon_1 - \epsilon_g$ at the same time, due to the Coulomb repulsion raising the energy cost of adding an electron to adjacent levels. This assumption is fine, but to be consistent we then also have to prohibit simultaneous occupation of the energy levels within a single quantum dot (ϵ_1 and ϵ_2, or $\epsilon_1 - \epsilon_g$ and $\epsilon_2 + \epsilon_g$), but this is something that the authors neglect in their description. In the next section we will address this inconsistency as well as other comments made on the refrigerator model after its publication.

4.2 DISCUSSION

When Cleuren *et al.* presented the model described in the previous section, many comments ([1] [6] [9] [16]) to the article were published and a discussion ensued. The violation of the third law of thermodynamics presents a problem that needs to be solved, and it is our opinion that the suggestions given in the comments are only methods to circumvent the problem by sim-

plifications of the model rather than real solutions. In this section I will present the main statements of the comments made on the article by other authors, and explain why we believe that the violation of the third law in this model is a problem that still needs to be solved.

In the proposed model the authors calculates that the cooling power of the refrigerator, $dQ_R/dt = \dot{Q}_R$, scales linearly with the temperature T_R of the "cold" reservoir in the limit of $T \to 0$. The heat-capacity of metals consists of a phonon contribution ($\propto T^3$) due to the vibration of the atoms, and an electronic contribution ($\propto T$) due to the motion of the electrons. At low temperatures the phonon heat capacity is negligible compared to the electronic, and the heat capacity is proportional to T. A. Levy *et al.* noticed that the refrigerator can not have a linear temperature dependence in both the cooling power and the heat capacity, without violating the unattainability statement of the third law of thermodynamics [16]. The model as presented by the authors predicts that the refrigerator can cool the right lead to absolute zero in a finite amount of time.

To see how the unattainability principle is broken, consider a general system with cooling power $\dot{Q}(T)$, and specific heat $C_v(T)$. Assume that C_v and $\dot{Q}$ scales with temperature according to powers of κ and λ respectively.

$$C_V(T) = \frac{dQ}{dT} \propto T^{\kappa}$$

$$\dot{Q}(T) = \frac{dQ}{dt} \propto T^{\lambda}$$

Now take the ratio between the heat capacity and the cooling power to obtain

$$\frac{\dot{Q}(T)}{C_V(T)} = \frac{dQ/dt}{dQ/dT} = \frac{dT}{dt} \propto T^{\kappa-\lambda} \tag{18}$$

Here dT/dt is considered the rate of temperature change of the system and according to the unattainability principle the powers are constrained by

$$\kappa - \lambda > 1 \tag{19}$$

and for the refrigerator system proposed the exponents are $\kappa = \lambda = 1$, in direct violation of the third law. To show why the powers are constrained in this way we let $\alpha = \kappa - \lambda$ and write

$$\frac{dT}{dt} = -AT^{\alpha} \tag{20}$$

We add the minus sign since in a cooling process $dT < 0$, and A is a positive constant. By integrating this equation we obtain

$$\int_{T}^{T_0} \frac{1}{T^\alpha} = \int_{t}^{t_0} -A\,dt \qquad \rightarrow \qquad \left[\frac{T^{1-\alpha}}{1-\alpha}\right]_{T}^{T_0} = -\Big[At\Big]_{t}^{t_0} + B \quad (21)$$

Here T_0 and t_0 is the initial temperature and time respectively, and B is an integration constant. We set $t_0 = 0$ and obtain

$$\frac{1}{1-\alpha}\left(T_0^{1-\alpha} - T^{1-\alpha}\right) = At + B \tag{22}$$

At $t = 0$ we have $T = T_0$, and thus $B = 0$. By isolating the expression for t we find

$$t = \frac{T_0^{1-\alpha} - T^{1-\alpha}}{A(1-\alpha)} \tag{23}$$

This equation tells us how long time t it takes to cool the system from temperature T_0 to temperature T. By taking the limit as $T \to 0$ of this equation we find that for $\alpha > 1$ the time it takes to cool the system is $t \to \infty$, in agreement with the third law. But if $\alpha < 1$ we find that t converges to

$$t = \frac{T_0^{1-\alpha}}{A(1-\alpha)} \tag{24}$$

which represents cooling to absolute zero in a finite amount of time, a violation of the third law. When considering the intermediate case where α is 1, we have to consider two limits as α can either approach 1 from below or above.

$$\lim_{\alpha\to 1^+}\lim_{T\to 0} \frac{T_0^{1-\alpha} - T^{1-\alpha}}{A(1-\alpha)} = -\infty \tag{25}$$

When approaching from above the terms in both the numerator and denominator causes $t \to -\infty$.

$$\lim_{\alpha\to 1^-}\lim_{T\to 0} \frac{T_0^{1-\alpha} - T^{1-\alpha}}{A(1-\alpha)} = 0 \tag{26}$$

By approaching from below the denominator causes the expression to go towards $+\infty$, but since the exponent goes faster towards 0 this behavior is suppressed and the end result is $t \to 0$. Thus we see that for all values of α less than or equal to 1, the

third law of thermodynamics is violated.

We previously introduced the unattainability principle in Chapter 2 as inability to cool any system to absolute zero, in a finite amount of steps. How the statement changes from "a finite amount of steps" to "a finite amount of time" is not entirely clear and something that needs to be addressed. Although intuition might tell us that there is a one-to-one relationship between a these statements, they are not equivalent. As long as we can either make the steps smaller, or the time needed to perform them shorter, as a function of temperature we will eventually be able to reach absolute zero in an finite amount of time even if there is an infinite amount of steps. To be able to perform an infinite amount of steps in a finite amount of time we require

$$\frac{\Delta T}{\Delta X} \to 0 \qquad \text{or equivalently} \qquad \frac{\Delta X}{\Delta T} \to \infty$$

where ΔT is the time required to perform one step, and ΔX is the step size. One can imagine a cooling process which requires an infinite amount of steps or cycles to reach absolute zero but as long as one could perform the cycles with increasing rate as a function of temperature one could reach absolute zero in a finite amount of time. It is thus not entirely clear to us how one transition from the finite amount of steps to the finite amount of time formulations of the unattainability principle. The empirical evidence for their equivalence is overwhelming, and although it has been proven for many specific systems there seems to be no general proof of this [33] [17]. We will nevertheless for the rest of this thesis take their equivalence as a fact.

A. Levy *et al.* were the first to notice the violation of the third law in the model, and published a comment [16]. They then suggest that a possible reason for the violation is that transitions between the lower and higher level within a single dot is ignored by the original authors. According to W. G. van der Wiel *et al.* [31] the photon-assisted tunnelling between quantum dots only produce a small tunnelling current which is comparable to the transition rate within a single dot, thus the internal transitions can not be ignored. They then propose a redefinition of the model, where one include the possibility of internal transitions in the quantum dots, e.g. from ϵ_1 to ϵ_2 or $\epsilon_2 + \epsilon_g$ and similar transitions. They go on to solve the new model analytically, and find that the condition for cooling ($\dot{Q}_r > 0$) can

not be simultaneously satisfied with the condition of zero net electrical current, while operating at the stationary state. A non-zero net electrical current in the device will cause a buildup of charge, stopping any further transfer of electrons, thus it is a crucial condition for the device to operate as a refrigerator.

In the reply to this comment B. Cleuren *et al.* [6] agrees that the third law is broken, but not by the method suggested in the comment. They simply state that the internal transitions of a single quantum dot can not be the cause, because one can imagine that there are four quantum dots, each with a only a single energy level in the relevant range, participating in the transport instead of two. One pair which transports hot electrons above the Fermi-level from the cold lead to the hot lead, and another pair for the transport in the opposite direction below the Fermi-level. Spatially separating the two pairs to a degree where internal transitions can be neglected completely solves the problem proposed by A. Levy *et al.*, thus the question of what causes the violation is still open.

O. Entin-Wohlman *et al.* consider in [9] an alternative and simpler version of the model by B. Cleuren *et al.*, where there is only two levels for transport between the metallic leads as in Fig. 1 of Ref. [12]. This corresponds to only the lower or upper electron pathway of our model. In Fig. 12 the model they

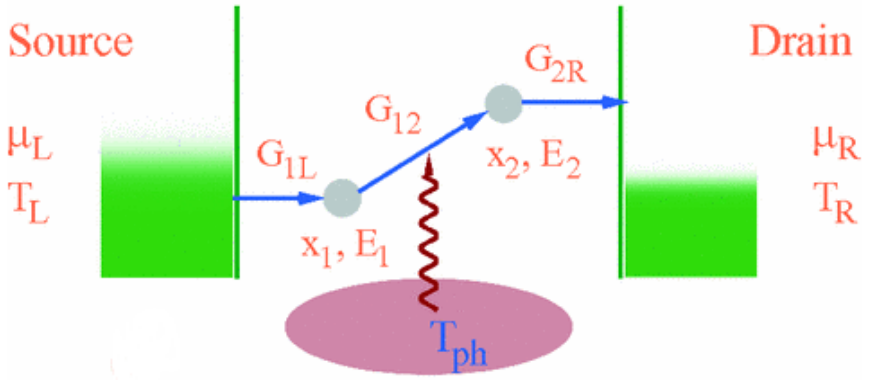

Figure 12: The single level model used in Ref.[12]. The physical situation is the same as in the model of B. Cleuren *et al.*, only here there is just a single channel of particle current.

consider is shown. An electron that leaves the left lead has a heat $E_1 - \mu$ associated with it. To cool the lead, we have to have

$E_1 - \mu > 0$. Using Fermi's golden rule they find that the particle current is proportional to the population of the lead, which is exponentially small for $kT << E_1 - \mu$. Thus the cooling power is quenched at very low T. However, what the authors neglect is that in the model the levels ϵ_1 and ϵ_2 are not static, but can be raised and lowered as needed by an external potential. Therefore one can always move the energy levels ϵ_1 and ϵ_2 as close as one wants to μ. We will see in Chapter 7 and 8, where we have performed calculations to optimize the cooling power for a whole range of temperatures, we find that this is exactly what happens; ϵ_1 and ϵ_2 will approach μ as the temperature is lowered.

Armen E. Allahverdyan *et al.* writes in Ref. [1] that they agree that the dynamic third law is broken, but that the proposal used by A. Levy is not the correct method to save the third law. They state that the function of a refrigerator can be found by taking limits, but one has to be careful to distinguish between two different types of asymptotic behavior.

1. Circumstantial limits which *strengthens* the characteristic behavior of the model.

2. Dysfunctional limits which *suppress* the desired function of the device.

They then suggests that the violation occurs due to a dysfunctional limit, which reduce the power of the refrigerator when applied for $T_R \to 0$. Since the model described in Ref. [5] is a Markovian system, detailed balance must be satisfied between the two metallic leads. The authors further states that according to Ref. [27] it is impossible for a system coupled to a heat bath to be in its pure ground provided the system-bath interaction Hamiltonian and its commutator with the full Hamiltonian is non-zero. The model described in Ref. [5] belongs to this class of refrigerators, and the only way to justify taking the limit $T \to 0$ is by simultaneously decreasing the coupling between the system and the bath, $\gamma \to 0$. However, for this system that limit can not be applied, since any refrigerator needs to have a finite coupling to its baths to produce a finite cooling power. The authors state that this argument is technically only valid for $T_L = T_R$, nevertheless there will be low T_R validity limits of the weak-coupling master equation also for when $T_R < T_L$. The coupling between the baths $\gamma \to 0$ will quench the cooling power proportionality $\dot{Q} \propto T_R$ when the master equation

is forced to apply for all $T_R \to 0$. We have had trouble understanding the difference between a circumstantial limit and a dysfunctional limit, and how it is relevant to the problem. Although they make good points, the authors fail to provide an explicit solution to the violation of the third law in this specific model. Of course if we take into account all quantum effects involved in the real system as it approaches absolute zero the description of the model will become quite different from the original. However it is our opinion that there must be a simpler solution, which requires the least amount of change in the assumptions of the original model.

4.3 NON-EQUILIBRIUM SYSTEMS AND THERMODYNAMICS

There are two important points to make when discussing this refrigerator model. Firstly, the system is clearly not in equilibrium; there is a temperature gradient between the reservoirs and energy is transferred between them. Earlier in Chapter 2 we learned that the third law is only valid for systems where all of the aspects of entropy are in internal equilibrium, so why is it surprising that a non-equilibrium refrigerator violates the third law? It is important to realize that one of the model assumptions is that when an electron is transferred between the cold left lead and the quantum dot, the metallic lead immediately equilibrate. As an example; when you move a cold electron from the left lead to the right lead, energy is instantly redistributed between all the electrons, such that energy is distributed according the Fermi-distribution. Thus the cold reservoir is always in equilibrium, and should obey the third law of thermodynamics.

Secondly, the flow of heat energy from cold to hot does not violate the second law of thermodynamics. We discussed in Chapter 3 that the second law is only valid when averaged over reasonable time-scales, so that it is possible for heat energy to flow from cold to hot without violating the third law as long as it can be considered a fluctuation. The flow of heat from cold to hot in this refrigerator model is neither a fluctuation, nor a violation of the second law. It is an open system which has work performed on it by the Sun which drives the heat-flux in the opposite direction of that which it would flow if the system was left to itself.

4.4 OBJECTIVE

The violation of the third law in the presented refrigeration model is a problem that needs to be solved. It is our opinion that none of the comments made in the discussions that followed its publication gives a satisfactory solution to this problem. Although good points were brought up, the commentators suggestions as to why the third law was broken consisted in either pointing out easily rectified problems or presenting similar but fundamentally different refrigerator systems where the third law is not violated. Our main objective to find out exactly which assumption made when describing the model causes the third law to be violated in this specific model without introducing changes that reduces it to an unrecognizable state. Once found we will make a suitable modification to better reflects the true nature of the system, and restore the third law of thermodynamics.

5

NON-EQUILIBRIUM THERMODYNAMICS

Thermodynamics is no longer about large steam machines and macroscopic systems in equilibrium. Very few things in nature are in equilibrium, for in equilibrium everything is static and nothing changes, while in nature change is all around us. With new experimental equipment developed during the last 20-30 years we are now able to measure and manipulate very small systems. Modern thermodynamics includes microscopic nanosystems, molecular motors and microbiological processes. These small systems have several features in common that results in fundamentally different behaviour than large macroscopic systems [21].

- Small systems are highly susceptible to perturbations, making it easy to bring them out of equilibrium. Perturbation theory and linear response theory have traditionally been used to solve problems with weak perturbations, however these theories fail far from equilibrium.
- In large systems the fluctuation of a parameter is usually negligible when compared to the average value. Thus the mean behaviour is enough the completely describe the system. In small systems however, fluctuations are large compared to the mean behaviour, which limits the amount of information contained in averaging the system parameters. A detailed description of the fluctuation is required to fully understand the system.
- In the limit of small systems and low temperatures quantum statistics may become relevant and coherent effects needs to be considered.

The phenomena observed at this scale requires theoretical explanations, and universal relations which are valid far from equilibrium needs to be developed. This is where stochastic thermodynamics comes into the picture. It is a relatively new branch of physics which has seen a lot of activity in the last 20 years. The dynamics of the systems considered are stochastic, i.e. the processes of the system are probability driven. The

initial stochastic formalism is very general and have uses in finance, biology, and sociology. In this chapter we will show that this stochastic mathematics under a few assumptions leads to thermodynamic results that we recognize as non-equilibrium analogues to their equilibrium definitions. The theoretical framework given in this chapter is based on the sources [21] and [10], and will be used explicitly in the next chapter to find the thermodynamic properties of the nano-refrigerator model introduced in Chapter 4.

5.1 THE STOCHASTIC MASTER EQUATION

The master equation is a tool used to describe the time evolution of the probability of a discrete set of states in a system. This type of equation is usually formulated in matrix form as in Eq.(27). Here p_m is the probability that the system is in state m, and M^ν is the rate matrix for processes via the reservoir denoted by ν. The rate matrix element $M^\nu_{m,m'}$ gives the probability to transition from state m' to state m, and it may have a time dependence due to an external driving force λ_t.

$$\dot{p}_m(t) = \sum_{m',\nu} M^\nu_{m,m'}(\lambda_t) p_{m'}(t) \tag{27}$$

Thus the master equation tells us how the probability of occupying state m evolves over time due to transitions to and from the other states m' of the system. In this form the master equation is a general mathematical concept, which can be applied to any stochastic process. A key property of the rate matrix M is that the sum of all row elements for each column is zero.

$$\sum_m M_{m,m'} = 0 \tag{28}$$

This is just a statement of conservation of probability. The result is that a given rate matrix M

$$M = \begin{bmatrix} M_{11} & M_{21} & M_{31} \\ M_{12} & M_{22} & M_{32} \\ M_{13} & M_{23} & M_{33} \end{bmatrix} \tag{29}$$

can be written in the following form.

$$M = \begin{bmatrix} -M_{12} - M_{13} & M_{21} & M_{31} \\ M_{12} & -M_{21} - M_{23} & M_{32} \\ M_{13} & M_{23} & -M_{31} - M_{32} \end{bmatrix} \tag{30}$$

The interpenetration is now that the diagonal elements represents the probability to remain in the same state, while off-diagonal elements are the probabilities of transition to the other states of the system.

5.2 LOCAL DETAILED BALANCE

By introducing the concept of local detailed balance, the master equation obtains a physical meaning and we end up with a stochastic description of thermodynamic system. In general detailed balance is the idea that in equilibrium a process/transition is reversed by its opposite process. Local detailed balance in this context is the assumption that the ratio of the probability of a transition from $m' \to m$ to the inverse transition $m \to m'$ is given by the Boltzmann factor for the difference in energy between the two states. The equation for local detailed balance is

$$\frac{M^{\nu}_{m,m'}(\lambda_t)}{M^{\nu}_{m',m}(\lambda_t)} = \exp\left(\frac{\epsilon_{m'}(\lambda_t) - \epsilon_m(\lambda_t)}{T^{\nu}}\right) \tag{31}$$

and it is the only thing we need to add to the formalism to give physical meaning to the master equation. For states with small energy differences the transition $m \to m'$ and its inverse transition $m' \to m$ are approximately equally likely.

Assuming there is no time dependence in the external driving force, i.e. the energy of the states in the system is constant through time, the system will reach a stationary state with $\dot{p}_m = 0$ where the occupation probability of all the states reach a constant time-independent value. The steady state master equation is then

$$\sum_{m',\nu} W^{\nu}_{m',m}(\lambda) p^{st}_{m'}(\lambda) = 0 \tag{32}$$

where the time dependent probability $p_m(t)$ is replaced by the stationary state probability $p^{st}_m(\lambda)$

$$p_m(t) \to p^{st}_m(\lambda)$$

If needed, we can also introduce a time dependence to the driving force, where we assume the rate of change is much smaller that the time it takes for the system to equilibrate.

$$p_m^{st}(\lambda) \to p_m^{st}(\lambda_t)$$

Thus the probability is always in a steady state for the relevant time scale of the system we are investigating.

5.3 THE STOCHASTIC LAWS OF THERMODYNAMICS

With Eq.(31) and Eq.(32) and the formalism laid out in the previous section, we are now prepared to formulate familiar equilibrium thermodynamic laws in a stochastic non-equilibrium framework.

5.3.1 *The First Law*

The total internal energy of a system $U(t)$ can be defined as the sum over all the energystates $\epsilon_m(\lambda_t)$ times its occupational probability $p_m(t)$ as shown in Eq.(33).

$$U(t) = \sum_m p_m(t)\epsilon_m(\lambda_t) \tag{33}$$

The energy is in thermodynamics naturally divided into two terms, work and heat. Similarly the energy change, $dU/dt = \dot{U}$, which is shown in Eq.(34) is divided into two parts which represents work and heat flux.

$$\dot{U}(t) = \sum_m p_m(t)\dot{\epsilon}_m(\lambda_t) + \sum_m \dot{p}_m(t)\epsilon_m(\lambda_t) \tag{34}$$

$$\dot{Q}(t) = \sum_m \dot{p}_m(t)\epsilon_m(\lambda_t) \qquad \dot{W}(t) = \sum_m p_m(t)\dot{\epsilon}_m(\lambda_t)$$

The first term of Eq.(34) Is the change of the total energy $U(t)$ due to the variation of the individual energy states $\epsilon_m(\lambda_t)$. These states vary depending ot the driving force λ_t thus it is natural to consider this term as work. The second term is the change of the total energy due to the stochastic transitions that change the occupation probabilities $p_m(t)$. These transitions are driven by the heat bath, thus this term represents heat.

$$\dot{U}(t) = \dot{W}(t) + \sum_\nu \dot{Q}^\nu(t) \tag{35}$$

We have to include the possibility of several heat baths, thus the first law takes the form shown in Eq.(35) where we sum over all the heat baths denoted ν. Next we replace the $\dot{p}_m(t)$ term in equation for heat flux with the master equation, Eq.(27), and obtain

$$\dot{Q}^{\nu}(t) = \sum_{m,m'} M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t) \Big(\epsilon_m(\lambda_t) - \epsilon_{m'}(\lambda_t) \Big) \tag{36}$$

The total heat flux from heat bath ν its thus the sum over all possible transitions $M_{m,m'}$, multiplied by their associated energy change $(\epsilon_m - \epsilon_{m'})$, and weighted by the occupation probabilities $p_{m'}$.

5.3.2 *The Second Law*

The probabilistic formulation of the Boltzmann entropy is given by

$$S(t) = -\sum_{m} p_m(t) \ln p_m(t) \tag{37}$$

The total entropy of a system is given by the probability to be in state m multiplied by its logarithm, summed over all possible states. To formulate the second law we take the derivative of $S(t)$ and obtain

$$\begin{aligned} \dot{S}(t) &= -\sum_{m} \Big[\dot{p}_m(t) \ln p_m(t) + \dot{p}_m \Big] \\ &= -\sum_{m,m',\nu} M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t) \ln p_m(t) \end{aligned} \tag{38}$$

where we replace $\dot{p}_m(t)$ by the master equation definition and realize that $\sum_m \dot{p}_m = 0$ due to the conservation of probability flow.

Now we invoke the local detailed balance assumptions of Eq.(31) and Eq.(32), and add and subtract the logarithm of Eq.(31), as well as adding $\ln p_{m'}(t)$ as shown in Eq.(39). We are also free to add

$$\sum_{m,m',\nu} M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t) \ln p_{m'}(t)$$

since only $M^{\nu}_{m,m'}$ depends on m in this expression and as we previously stated $\sum_m M^{\nu}_{m,m'} = 0$. With these considerations we obtain

$$\dot{S}(t) = -\sum_{m,m',\nu} M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t) \left[\ln \frac{M^{\nu}_{m,m'}(\lambda_t)}{M^{\nu}_{m',m}(\lambda_t)} - \ln \frac{M^{\nu}_{m,m'}(\lambda_t)}{M^{\nu}_{m',m}(\lambda_t)} + \ln p_m(t) - \ln p_{m'}(t) \right] \tag{39}$$

In stochastic thermodynamics one differentiates between two types of entropy change; the entropy flow $\dot{S}_e$, and the entropy production $\dot{S}_i$. These two terms can be differentiated and separated using Eq.(39). The entropy flow is given in Eq.(40), and it measures the entropy exchange between the system and the heat baths. The total entropy of the heat bath and the system is conserved in this exchange, and thus it is considered the reversible contribution to the change of entropy of the system.

$$\dot{S}_e(t) = -\sum_{m,m',\nu} M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t) \ln \frac{M^{\nu}_{m,m'}(\lambda_t)}{M^{\nu}_{m',m}(\lambda_t)} = \sum_{\nu} \frac{\dot{Q}^{\nu}(t)}{T_{\nu}} \tag{40}$$

Where we use have used

$$\ln \frac{M^{\nu}_{m,m'}(\lambda_t)}{M^{\nu}_{m',m}(\lambda_t)} = \frac{\epsilon_{m'}(\lambda_t) - \epsilon_m(\lambda_t)}{T^{\nu}}$$

which makes us able to rewrite the entropy flow with respect to the heat flux from reservoir ν according to Eq.(36). The second term of Eq.(39) is thus the entropy production, which measures the amount of irreversible entropy change.

$$\dot{S}_i(t) = \sum_{m,m',\nu} M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t) \ln \frac{M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t)}{M^{\nu}_{m',m}(\lambda_t) p_m(t)} \geqslant 0 \tag{41}$$

If we consider two expressions for entropy change, we see that the only difference is in the logarithm. For $\dot{S}_e(t)$ the term in the logarithm is just the local detailed balance, while for $\dot{S}_i(t)$ the term in the logarithm is a measure the irreversible entropy increase of the system associated with a transition between the state m' and m. In order to have a reversible transformation the entropy production has to be zero. This can only happen when the ratio of the logarithm in Eq.(41) is 1, i.e. when

$$M^{\nu}_{m,m'}(\lambda_t) p_{m'}(t) = M^{\nu}_{m',m}(\lambda_t) p_m(t)$$

for all m, m' and ν, which is the global equilibrium condition.

The final expression for the change in entropy is thus given by the sum of entropy flow and entropy production as shown below in Eq.(42), and can be recognized as the stochastic definition of the second law of thermodynamics.

$$\dot{S}(t) = \dot{S}_e(t) + \dot{S}_i(t) = \sum_{\nu} \frac{\dot{Q}^{\nu}(t)}{T_{\nu}} + \dot{S}_i(t) \geqslant 0 \tag{42}$$

Assuming there are no gradients in the thermodynamic properties of the reservoirs of the system, and thus are in a state of global equilibrium where detailed balance is satisfied, we have zero entropy production and a steady state.

$$M^{\nu}_{m,m'}(\lambda) p^{s}_{m'} = M^{\nu}_{m',m}(\lambda) p^{st}_{m}(\lambda) \quad \rightarrow \quad \dot{S}_i = 0 \tag{43}$$

On the other hand, if there are thermodynamic gradients between the reservoirs the global detailed balance is broken. Then the system transformations are non-reversible, and we have a finite entropy production in this non-equilibrium steady state.

$$M^{\nu}_{m,m'}(\lambda) p^{st}_{m'} \neq M^{\nu}_{m',m}(\lambda) p^{st}_{m}(\lambda) \quad \rightarrow \quad \dot{S}_i \neq 0 \tag{44}$$

It can also be shown that the steady state occupation probability is equal to the equilibrium distribution of the canonical ensemble

$$p^{st}_{m}(\lambda) = \frac{exp(-\epsilon_m(\lambda)/T)}{Z(\lambda)} \tag{45}$$

where $Z(\lambda)$ is the canonical partition function

$$Z(\lambda) = \sum_{m} exp(-\epsilon_m(\lambda)/T)$$

.

5.4 TIGHT COUPLING AND EFFICIENCY

We now consider an open system, where both energy and particles can be exchanged between the reservoirs and the system. Every transition is thus associated with a change in the number of particles N_m in state m, and the number of particles $N_{m'}$ in state m', in addition to the change in energy $\epsilon_{m'} - \epsilon_m$ as before.

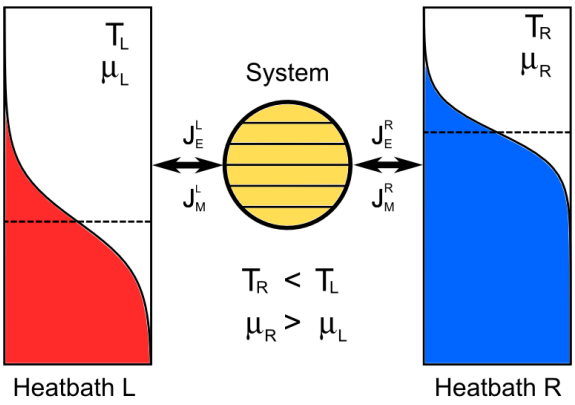

Figure 13: Schematic of an open system connected to two heat-baths. In this example the temperature of heat-bath R (T_R) is lower than that of heat-bath L (T_L), while its chemical potential is higher ($\mu_R > \mu_L$). The system is open and can freely exchange energy and particles between the two heat-baths. The horizontal lines within the system represent discrete states of energy, which in this case is time-independent.

By expanding the local detailed balance equation to include the energy change associated with the change in particle numbers, we obtain

$$\frac{M^{\nu}_{m,m'}}{M^{\nu}_{m',m}} = \exp\{-\beta_\nu \left[(\epsilon_m - \epsilon_{m'}) - \mu_\nu (N_m - N_{m'})\right]\} \tag{46}$$

In equilibrium this leads to the grand canonical distribution, where we earlier had the canonical distribution. The energy current and matter current is defined respectively as in Eq.(47) and Eq.(48). It is just the transition rate $m \to m'$ multiplied by the energy/particle number difference between the two states.

$$J_E(t) = \sum_{m,m'} M_{m,m'} p_{m'}(t)\left(\epsilon_m - \epsilon_{m'}\right) \tag{47}$$

$$J_M(t) = \sum_{m,m'} M_{m,m'} p_{m'}(t)\left(N_m - N_{m'}\right) \tag{48}$$

The total heat flux from reservoir ν can thus be written as the sum of the matter and energy current.

$$\dot{Q}^{\nu}(t) = J^{\nu}_E(t) - \mu_\nu J^{\nu}_M(t) \tag{49}$$

We now consider a system connected to two reservoirs denoted R and L (for left and right) where $T_R \leqslant T_R$ and $\mu_R \geqslant \mu_L$ as

shown in Fig.(13). In the steady state where $\dot{p}_m = 0$ the system between the two reservoirs does not change and thus the energy and matter current out of reservoir R must be the same as the energy and matter current into reservoir L, i.e. the energy and particle flow is conserved.

$$J^r_{M,E} = -J^l_{M,E} = J_{M,E} \tag{50}$$

The power P is defined as the derivative of the work, which is equal to the sum of all the heat fluxes, $\dot{Q}^\nu$ in the steady state where the change in energy is zero. The power is thus the matter current J_M multiplied by the difference in chemical potential between the two reservoirs.

$$P = -\dot{W} = \sum_\nu \dot{Q}^\nu(t) = -(\mu_L - \mu_R)J_m \tag{51}$$

Now in the steady state the total entropy change $\dot{S}$ is zero since it is a state function that only depends on $\dot{p}_m$ (see Eq.(38)), which is time-independent.

$$\dot{S} = \dot{S}_i + \dot{S}_e = 0 \quad \rightarrow \quad \dot{S}_i = -\dot{S}_e$$

$$\dot{S}_i = -\sum_\nu \frac{\dot{Q}^\nu(t)}{T_\nu} = (\frac{1}{T_R} - \frac{1}{T_L})J_E + (-\frac{\mu_R}{T_R} + \frac{\mu_L}{T_L})J_M \tag{52}$$

By introducing the thermodynamic forces F_E and F_M, the entropy production can be rewritten as a flux multiplied by a force.

$$\dot{S}_i = -\dot{S}_e = F_E J_E + F_M J_M \geqslant 0 \tag{53}$$

The thermodynamic forces, F_E and F_M, are themselves associated with energy and matter transfer respectively and are defined as

$$F_E = \frac{1}{T_R} - \frac{1}{T_L} \qquad F_M = -\frac{\mu_R}{T_R} - (-\frac{\mu_L}{T_L}) \tag{54}$$

The thermodynamic efficiency η is the ratio between the work output ($-W \geqslant 0$) and the heat extracted from the hot reservoir ($Q^L \geqslant 0$). Since we have $\dot{W} = T_R\dot{S}_i - \eta_C Q^L$, where η_C is the Carnot efficiency defined as

$$\eta_C = 1 - \frac{Tl}{T_r}$$

we can write the efficiency of the system as

$$\eta = \frac{-W}{Q^L} = \eta_C - \dot{S}_i \frac{T_R}{\dot{Q}^L} \tag{55}$$

We see that the efficiency is equal to the Carnot efficiency minus a term involving the entropy production, which is always greater than or equal to zero, and thus

$$0 \leqslant \eta \leqslant \eta_C$$

If the system is in equilibrium, where the entropy production is zero, we have $\eta = \eta_C$. From Eq.(53) we see that this implies that $F_E J_E = -F_M J_M$. In general this is only satisfied when all the thermodynamic gradients goes to zero, i.e. $F_E, F_M \Longrightarrow 0$. This results in a Carnot efficiency $\eta_C = 0$ and a power $P = 0$, thus there can be no useful work extracted.

The efficiency can also be written in terms of the chemical potentials and energy/matter currents as follows

$$\eta = \frac{-W}{Q^L} = \frac{-\dot{W}}{\dot{Q}^L} = \frac{-(\mu_L - \mu_R)J_M}{J_E - \mu_L J_M} = \frac{\mu_L - \mu_R}{\mu_L - J_E/J_M} \tag{56}$$

Observe that if we make the energy current proportional to the matter current, η will be independent of all the currents and only depend on the system parameters.

$$\dot{S}_i = FJ \tag{57}$$

$$J \equiv J_E = \gamma J_M \rightarrow \qquad F = F_M + \gamma F_E \tag{58}$$

$$\eta = \frac{\mu_R - \mu_L}{\gamma - \mu_L} \tag{59}$$

Here γ is some coupling constant. This linear coupling between the matter current and energy current is referred to as a tight coupling, and it implies that the particle itself is the carrier of energy in the system. The tight coupling makes it possible for the entropy production $\dot{S}_i$ to be zero even though the thermodynamic forces are non-zero. For $\dot{S}_i = 0$ requires that $F = 0$, but F can be zero while F_M and F_E is non-zero. This results in a remarkable situation where the system has thermodynamic gradients ($T_R \neq T_L$ and $\mu_R \neq \mu_L$), yet is in a state of equilibrium with zero entropy production. However, since the system is in equilibrium the power and efficiency is zero and we have to move into the realm of non-equilibrium the obtain any useful work from the system.

6

BOSON POWERED REFRIGERATION

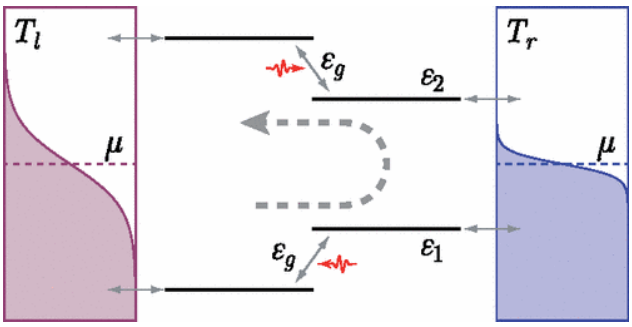

Figure 14: Schematic of the refrigerator. Left side is the hot lead, and right side is a cold lead. The two leads are connected by two quantum dots. The Fermi-level is marked by μ, and the gray arrow shows the direction of electron transport. Illustration taken from B. Cleuren *et al.*[5].

In this chapter, we will use the formalism developed in the previous chapter to study the thermodynamic properties of the boson powered nano-refrigerator we introduced in Chapter 4. This work was first done by the authors of [5], and here we will reproduce their results. The goal is to understand how to optimize the efficiency of the cooling process, and study the potential for cooling at very low temperatures. We will find that the assumptions made when creating this model results in a violation of the unattainability principle, and the rest of the thesis will concern itself with understanding the cause of this violation and how to correctly describe the refrigerator system in accordance with the third law of thermodynamics.

6.1 PARTICLE CURRENTS

The electron transition rate between the leads and the quantum dots is proportional to the Fermi distribution occupation probability of the corresponding energy level in the lead. Elastic transition from the lead to an unoccupied dot can only happen if there is an electron in the metal with the exact same energy as the available level in the dot. Similarly, transition from an occupied dot to the lead can only happen if there is an available state in the Fermi-distribution, $f(\epsilon)$, of the metal with the

exact same energy as the electron in the quantum dot. Thus the transition rates between the dot and lead can be written as

$$k^{\epsilon}_{l\to d} = \Gamma f(\epsilon) \tag{60a}$$
$$k^{\epsilon}_{d\to l} = \Gamma\left(1 - f(\epsilon)\right) \tag{60b}$$
$$f(\epsilon) = \frac{1}{e^{(\epsilon-\mu)/k_B T} + 1}$$

where Γ is a material dependent constant which determines timescale of the transitions. In the equations $k_{l\to d}$ is the transition rate going from the leads to the dot, and $k_{d\to l}$ is for the opposite direction.

For the transitions between the two quantum dots, the incoming solar photons provide the energy required, ϵ_g, for the electron to jump between the energy levels. The number of solar photons with that energy can be found by using the Bose-Einstein distribution, $n(\epsilon_g)$.

$$k^{\epsilon_g}_{\uparrow} = \Gamma_s n(\epsilon_g) \tag{61a}$$
$$k^{\epsilon_g}_{\downarrow} = \Gamma_s\left(1 + n(\epsilon_g)\right) \tag{61b}$$
$$n(\epsilon_g) = \frac{1}{e^{\epsilon_g/k_B T_S} - 1}$$

In the equations above $k_{\uparrow}(\epsilon_g)$ is the transition rate when moving from a lower level to a higher level (for example from ϵ_2 to $\epsilon_2 + \epsilon_g$), whereas $k_{\downarrow}(\epsilon_g)$ is when moving from a higher to a lower level which includes stimulated emissions. Again the constant Γ_S is a material dependent term which determines the timescale of the transitions.

The particle current $J_1(J_2)$ between energy level $\epsilon_1(\epsilon_2)$ and the right lead is given in terms of the probabilities P_0 of finding no electron in the quantum dots and P_L or P_R for finding an electron in the left or right energy level respectively, and the transition rates listed above.

$$J_1 = P^1_R\, k^{\epsilon_1}_{d\to l} - P^1_0\, k^{\epsilon_1}_{l\to d} \tag{62}$$

$$J_2 = P^2_R\, k^{\epsilon_2}_{d\to l} - P^2_0\, k^{\epsilon_2}_{l\to d} \tag{63}$$

If we set $\mu = 0$ and consider the symmetric system, where $\epsilon_2 = -\epsilon_1 = \epsilon$, the equations for the particle currents J_1 and J_2 are

$$J_1 = P_R\Gamma\left(1 - \frac{1}{e^{-\epsilon/T_r}+1}\right) - P_0\Gamma\left(\frac{1}{e^{-\epsilon/T_r}+1}\right)$$

$$J_2 = P_R\Gamma\left(1 - \frac{1}{e^{+\epsilon/T_r}+1}\right) - P_0\Gamma\left(\frac{1}{e^{+\epsilon/T_r}+1}\right)$$

By taking the limit as T_R goes to zero, with ϵ constant, we obtain the following expression for $\dot{Q}_R$.

$$\lim_{T_R\to 0}\dot{Q}_R = \lim_{T_R\to 0}\epsilon\,(J_1 - J_2) = -\epsilon\,\Gamma\,(P_0 + P_R)$$

When ϵ is independent of temperature, this expression for $\dot{Q}_R$ is always negative. Since $\dot{Q}_R$ is defined as positive for heat flow *out of* the right lead, this statement is equivalent to prohibiting any cooling of the right lead at low temperatures. We conclude that in order for the refrigerator model to produce cooling power at low temperatures, we need to dynamically vary ϵ as a function of temperature, i.e.

$$\epsilon \to \epsilon(T_R)$$

In Chapter 5 we introduced the master equation, and its rate matrix as

$$\dot{p}_m(t) = \sum_{m',\nu} M^{\nu}_{m,m'}(\lambda_t)p_{m'}(t) \tag{64}$$

Using the equations for transition rates given in Eq.(60) and Eq.(61) we can construct a master equation that describe the transitions between the states of the lower transport channel (J_1).

$$\begin{bmatrix}\dot{P}^1_0\\ \dot{P}^1_L\\ \dot{P}^1_R\end{bmatrix} = \begin{bmatrix}-k^{\epsilon_2+\epsilon_g}_{l\to d} - k^{\epsilon_2}_{l\to d} & k^{\epsilon_2+\epsilon_g}_{d\to l} & k^{\epsilon_2}_{d\to l}\\ k^{\epsilon_2+\epsilon_g}_{l\to d} & -k^{\epsilon_2+\epsilon_g}_{d\to l} - k_\downarrow & k_\uparrow\\ k^{\epsilon_2}_{l\to d} & k_\downarrow & -k^{\epsilon_2}_{d\to l} - k_\uparrow\end{bmatrix}\begin{bmatrix}P^1_0\\ P^1_L\\ P^1_R\end{bmatrix} \tag{65}$$

A similar matrix can be constructed for the upper channel (J_2). We are interested in the steady state solution where $\dot{P}^1_R, \dot{P}^1_L, \dot{P}^1_0 = 0$. Only two of the rows of the matrix are linearly independent, one redundant equation thus needs to be replaced by the total

probability $P_0 + P_L + P_R = 1$. We write $P_0 = 1 - P_L - P_R$ and replace the first row of Eq.(65) to obtain

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 \\ k_{l\to d}^{\epsilon_1-\epsilon_g} & -k_{d\to l}^{\epsilon_1-\epsilon_g} - k_\uparrow & k_\downarrow \\ k_{l\to d}^{\epsilon_1} & k_\uparrow & -k_{d\to l}^{\epsilon_1} - k_\downarrow \end{bmatrix} \begin{bmatrix} P_0^1 \\ P_L^1 \\ P_R^1 \end{bmatrix} \tag{66}$$

By solving the matrix equation shown in Eq.(66), we obtain the explicit steady state probabilities P_0^1 and P_R^1 as a function of the temperatures T_R, T_L and T_S, and the energies ϵ and ϵ_g. Inserting this into Eq.(62) we also obtain an explicit solution for the particle current J_1 through the lower channel. Repeating this procedure for the upper transport channel we also find an explicit solution for the steady state particle current J_2. The full equations for the particle currents are given by

$$J_1 = \frac{\Gamma\Gamma_s(e^{X_R^1} - e^{X_L^1+x_S})}{(\Gamma_s+\Gamma)e^{X_R^1+X_L^1+x_S} + (\Gamma_s+\Gamma)e^{X_R^1+x_S} + (\Gamma_s-\Gamma)e^{X_R^1+X_L^1} + (2\Gamma_s+\Gamma)e^{X_L^1+x_S} + (2\Gamma_s-\Gamma)e^{X_R^1} + (\Gamma_s-\Gamma)e^{X_L^1} + 2\Gamma_s e^{x_S} + 2\Gamma_s} \tag{67}$$

and

$$J_2 = \frac{\Gamma\Gamma_s(e^{X_R^2+x_S} - e^{X_L^2})}{(\Gamma_s+\Gamma)e^{X_R^2+X_L^2+x_S} + (\Gamma_s+\Gamma)e^{X_L^2+x_S} + (\Gamma_s-\Gamma)e^{X_R^2+X_L^2} + (2\Gamma_s+\Gamma)e^{X_R^2+x_S} + (2\Gamma_s-\Gamma)e^{X_L^2} + (\Gamma_s-\Gamma)e^{X_R^2} + 2\Gamma_s e^{x_S} + 2\Gamma_s} \tag{68}$$

In these equations we have used the following substitutions for easier reading:

$$\begin{aligned} X_S &= \epsilon_g/T_s \\ X_R^1 &= (\epsilon_1 - \mu)/T_r \\ X_L^1 &= (\epsilon_1 - \epsilon_g - \mu)/T_l \\ X_R^2 &= (\epsilon_2 - \mu)/T_r \\ X_L^2 &= (\epsilon_2 + \epsilon_g - \mu)/T_l \end{aligned}$$

6.2 HEAT TRANSPORT AND EFFIECIENCY

When an electron moves from the right lead to the upper energy level ϵ_2 the internal energy of the right lead is effectively reduced by $dQ = \epsilon_2 - \mu > 0$. Similarly the electrons moving from the lower energy level ϵ_1 to the right lead brings with it a heat contribution of $dQ = \epsilon_1 - \mu < 0$, thus cooling the lead. This result comes from the first law of thermodynamics in the following form

$$dU = TdS - pdV + \mu dN$$

Assuming the mechanical work is zero we obtain

$$TdS = dQ = dU - \mu dN$$

With J_1 and J_2 as defined earlier, we can now obtain the following results for the steady state heat fluxes $\dot{Q}_R$, $\dot{Q}_L$ and $\dot{Q}_S$ from the right lead, the left lead and the Sun respectively.

$$\dot{Q}_R = (\epsilon_1 - \mu)(-J_1) + (\epsilon_2 - \mu)(-J_2) \tag{69a}$$
$$\dot{Q}_L = (\epsilon_1 - \epsilon_g - \mu)(J_1) + (\epsilon_2 + \epsilon_g - \mu)(J_2) \tag{69b}$$
$$\dot{Q}_S = \epsilon_g J_1 + \epsilon_g(-J_2) \tag{69c}$$

Conservation of energy is guaranteed from these equations as

$$\dot{Q}_R + \dot{Q}_L + \dot{Q}_S = 0$$

When writing the conservation law as the sum of all the heat-fluxes we neglect the energy input from the work performed on the system by dynamically moving the energy levels ϵ_1 and ϵ_2 as a function of temperature. The assumption that the work performed on the system is negligible when compared to the heat-fluxes is not hard to believe; one can always tune the parameters of the model in such a way that the particle currents and thus the heat-fluxes are much larger than the work required to move the energy levels. It is nevertheless important to be aware of this assumption, which is not mentioned during the proposition of the model by B. Cleuren *et al.* in [5].

The coefficient of performance for a general refrigerator is given by

$$\eta = \frac{\dot{Q}_C}{\dot{Q}_H - \dot{Q}_C}$$

where Q_C is the heat removed **from** the cold reservoir and Q_H is the heat supplied **to** the hot reservoir. For our system the cold reservoir is the right lead, and the hot reservoir is the left lead. We defined $\dot{Q}_{R/L}$ as the heat flux **from** the leads to the device, thus $\dot{Q}_C = \dot{Q}_R$ and $\dot{Q}_H = -\dot{Q}_L$. Conservation of energy gives $\dot{Q}_S = -\dot{Q}_R - \dot{Q}_L$. Thus we obtain the efficiency of the refrigerator as

$$\eta = \frac{\dot{Q}_R}{(-\dot{Q}_L) - \dot{Q}_R} = \frac{\dot{Q}_R}{\dot{Q}_S} \tag{70}$$

The entropy of the system remains constant during a steady state operation. The heat exchange with the three reservoirs results in an irreversible entropy production, $\dot{S}_i > 0$, in the device. Using the results we obtained in Chapter 5, we know that in the steady state the total entropy change in the system is zero, $\dot{S} = \dot{S}_i + \dot{S}_e = 0$. Thus the entropy produciton is equal to the negative of the entropy flow, or $\dot{S}_i = -\dot{S}_e$. According to Eq.(52), the entropy production can thus be written in terms of the heat-fluxes as

$$\dot{S}_i = -\frac{\dot{Q}_S}{T_S} - \frac{\dot{Q}_R}{T_R} - \frac{\dot{Q}_L}{T_L} \geqslant 0 \tag{71}$$

where

$$\dot{Q}_S > 0 \qquad \dot{Q}_R > 0 \qquad \dot{Q}_L < 0$$

Conservation of energy, $\dot{Q}_R + \dot{Q}_L + \dot{Q}_S = 0$, can now be used to rewrite this equation in the following form:

$$\begin{aligned}
\dot{S}_i &= -\frac{\dot{Q}_S}{T_S} - \frac{\dot{Q}_R}{T_R} - \frac{\dot{Q}_L}{T_L} \\
\dot{S}_i &= -\frac{\dot{Q}_S}{T_S} - \frac{\dot{Q}_R}{T_R} + \frac{\dot{Q}_S + \dot{Q}_R}{T_L} \\
\dot{S}_i &= \frac{\dot{Q}_S}{T_L} - \frac{\dot{Q}_S}{T_S} + \frac{\dot{Q}_R}{T_L} - \frac{\dot{Q}_R}{T_R} \\
\dot{S}_i &= \dot{Q}_S\left(\frac{1}{T_L} - \frac{1}{T_S}\right) + \dot{Q}_R\left(\frac{1}{T_L} - \frac{1}{T_R}\right) \\
\dot{S}_i &= \dot{Q}_S F_S + \dot{Q}_R F_R
\end{aligned} \tag{72}$$

Here we have defined the thermodynamic forces F_S and F_R

$$F_S = \frac{1}{T_L} - \frac{1}{T_S}$$

$$F_R = \frac{1}{T_L} - \frac{1}{T_R}$$

Since we have $T_R \leqslant T_L < T_S$, the range of these forces is $F_S > 0$ and $F_R \leqslant 0$. By rearranging Eq.(72) to isolate $\dot{Q}_R$ we obtain

$$\dot{Q}_R = (\dot{S}_i - \dot{Q}_S F_S)\frac{1}{F_R} \tag{73}$$

which can be inserted into the equation for the efficiency given in Eq.(70). The result is the following equation for the efficiency

of the refrigerator as a function of the temperatures T_L, T_R, T_S, the heat-flux from the Sun $\dot{Q}_S$ and the irreversible entropy production $\dot{S}_i$.

$$\eta = \frac{\dot{S}_i - \dot{Q}_S F_S}{Q_S F_S} = \frac{\dot{S}_i}{\dot{Q}_S F_R} - \frac{F_S}{F_R}$$
$$\eta = \frac{\dot{S}_i (T_R T_L)}{\dot{Q}_d (T_R - T_L)} - \frac{(T_S - T_L) T_R T_L}{(T_R - T_L) T_S T_L}$$
$$\eta = \left(-\frac{\dot{S}_i}{\dot{Q}_S} - \frac{T_L - T_S}{T_S T_L} \right) \left(\frac{T_R T_L}{T_L - T_R} \right)$$
$$\eta = \left(1 - \frac{T_L}{T_S} - \frac{\dot{S}_i T_L}{\dot{Q}_S} \right) \left(\frac{T_R}{T_L - T_R} \right) \tag{74}$$

This expression for the coefficient of performance can be interpreted as a Carnot efficiency of a heat engine operating between the two reservoirs at temperature T_S and T_L reduced by a factor $\dot{S}_i T_L / \dot{Q}_S$. The Carnot efficiency is then modified by the maximal COP for a refrigerator driven by a reversible work source and operating between the temperatures T_R (low temperature reservoir) and T_L (high temperature reservoir). The overall efficiency of the combined heat engine/refrigerator is maximized when the operation is reversible, i.e. when the entropy production, $\dot{S}_i$, is zero.

A trivial solution with zero entropy production is if the system is in total equilibrium ($T_R = T_L = T_S$) and the thermodynamic forces vanishes. This situation is however of no practical interest. A second solution can be found by fine-tuning the device parameters. First we make the heat currents proportional to each other by setting the chemical potential μ equal to $(\epsilon_1 + \epsilon_2)/2$ or equal to the chemical potential μ' where the particle current in the lower levels and higher levels cancels each other and the total particle current $J_1 + J_2$ vanishes. In both cases we obtain

$$\dot{Q}_R = \frac{\epsilon_2 - \epsilon_1}{2} (J_1 - J_2) \tag{75a}$$
$$\dot{Q}_L = \left(\frac{\epsilon_1 - \epsilon_2}{2} - \epsilon_g \right) (J_1 - J_2) \tag{75b}$$
$$\dot{Q}_S = \epsilon_g (J_1 - J_2) \tag{75c}$$

We observe that the heat fluxes are now proportional to each other. The proportionality between the power output $\dot{Q}_R$ and

the input energy $\dot{Q}_S$ is called a tight coupling. We introduced the concept in Chapter 5 as a coupling between the matter and energy current in a device such that $J_E = \nu J_M$ where ν is a proportionality constant. We see that if $\dot{Q}_R = \nu \dot{Q}_S$ the efficiency becomes

$$\eta = \frac{\dot{Q}_R}{\dot{Q}_S} = \frac{\epsilon_2 - \epsilon_1}{2\epsilon_g} \tag{76}$$

where the COP is dependent of the particle currents J_1 and J_2. Since the COP is no longer dependent on J_1 and J_2 the reversible regime can be reached while maintaining a non-zero COP, even when both $\dot{Q}_R$ and $\dot{Q}_S$ vanish. Rewriting the entropy production from Eq.(72) as $\dot{S}_i = \dot{Q}_S(F_S + \eta F_R)$, and isolating the expression for η, we obtain

$$\eta = \frac{1}{F_R}\left(\frac{\dot{S}_i}{\dot{Q}_S} - F_S\right) \tag{77}$$

Substituting η for Eq.(76) we find that the maximal efficiency ($\dot{S}_i = 0$) is reached when

$$\epsilon_g \left(1 - \frac{T_L}{T_S}\right) = \frac{\epsilon_2 - \epsilon_1}{2} \left(\frac{T_L - T_R}{T_R}\right) \tag{78}$$

6.3 COOLING POWER IN THE LIMIT OF ABSOLUTE ZERO

The Sun operates as an energy source which drives a heat flow from the cold lead towards the hot lead. For this to work, we require $\dot{Q}_R > 0$ or $\eta > 0$. And since both leads have the same chemical potential, we also have $T_S \geqslant T_L \geqslant T_R$. For a strongly coupled device the entropy production has to be greater than or equal to zero. We have $\dot{S} = \dot{Q}_S(F_S + \eta F_R) \geqslant 0$, and since $\dot{Q}_S > 0$ we obtain $F_S + \eta F_R \geqslant 0$. These conditions places a constriction on the range of the COP which is given by

$$0 \leqslant \frac{\epsilon_2 - \epsilon_1}{2\epsilon_g} \leqslant \left(1 - \frac{T_L}{T_S}\right)\left(\frac{T_R}{T_L - T_R}\right) \tag{79}$$

By noting that μ only appears as $\epsilon_1 - \mu$ or $\epsilon_2 - \mu$ we can set $\mu = 0$ and measure ϵ_1 and ϵ_2 with respect to this origin. Here the authors choose to analyze the model under the assumption that $\mu = (\epsilon_1 + \epsilon_2)/2$, and by setting the chemical potential to

zero we thus obtain $\epsilon_2 = -\epsilon_1 = \epsilon$, where $\epsilon > 0$. We stated earlier that the fine-tuning required that we make the heat fluxes $\dot{Q}_R$, $\dot{Q}_L$ and $\dot{Q}_S$ proportional to each other, and this could be done either by choosing $\mu = (\epsilon_1 + \epsilon_2)/2$ or $J_1 + J_2 = 0$. In the following calculations the total particle current $J_1 + J_2$ is thus non-zero and the right lead will be charged during the cooling process. The electrical charging of the right lead will change its chemical potential such that $\mu_R \neq \mu_L$ and the following derivations will be incorrect. The charging effect is not taken into consideration by the authors, but it is an important property that one needs to be aware of if we wish to someday build a real working quantum refrigerator. There is a quick fix for this problem though; we assume there is a capacitive system connected to the right lead, which we can use to remove or add electrons to keep $\mu_R = \mu_L$.

By including this additional assumption, Eq.(79) can then be rewritten as

$$\epsilon = \gamma \left(1 - \frac{T_L}{T_S}\right) \left(\frac{T_R}{T_L - T_R}\right) \epsilon_g \tag{80}$$

where $0 \leqslant \gamma < 1$ to ensure that the device operates within the conditions previously imposed. We now want to investigate the behavior of the device as $T_R \to 0$. When we make the energy levels ϵ_1 and ϵ_2 symmetric about the chemical potential, the heat-flux $\dot{Q}_R$ is given by

$$\dot{Q}_R = \epsilon(J_1 - J_2) \tag{81}$$

and by inserting our equation for ϵ we finally obtain the cooling power as a function of the temperatures and the particle currents.

$$\dot{Q}_R = \gamma \left(1 - \frac{T_L}{T_S}\right) \left(\frac{T_R}{T_L - T_R}\right) \epsilon_g (J_1 - J_2) \tag{82}$$

By taking the limit of this equation as $T_R \to 0$ we find that the particle current term $(J_1 - J_2)$ converges to a small positive number, such that the temperature dependence of $\dot{Q}_R$ becomes

$$\dot{Q}_R \propto T_R \tag{83}$$

As explained in Chapter 4, this linear temperature dependence of the system breaks the third law of thermodynamics. Since

the heat capacity, C_V, of a metal at low temperature is also linearly dependent on T_R, we obtain

$$\frac{dT}{dt} = \frac{\dot{Q}_R}{C_V} = A$$

where A is a constant, and the unattainability statement of the third law of thermodynamics is broken. In the following chapters we will find out exactly why the third law is violated, and how we can modify the model to restore it.

7

NUMERICALLY OPTIMIZED COOLING

In this chapter we analyze the boson-refrigerator by numerical modeling. As explained in the previous chapter, we have to continuously adjust the energy levels of the quantum dots as a function of temperature in order to operate within the window of refrigeration. The authors define a variable $\gamma \in [0, 1]$ and calculate that the value of ϵ that returns the highest cooling power is given by

$$\epsilon = \gamma \left(1 - \frac{T_l}{T_s}\right) \left(\frac{T_r}{T_l - T_r}\right) \epsilon_g \tag{84}$$

This equation only tells within which range we can find the optimal ϵ, but it is used to show that the cooling power $\dot{Q}_R$ is proportional to T_R. As we understand it, γ can in principle also depend on the temperature T_R. So in this chapter we want to reproduce the linearity of $\dot{Q}_R$ with respect to T_R without relying on the introduction of the factor γ, as we believe the argument presented by the authors are unconvincing.

7.1 CONDITIONS FOR OPTIMIZED COOLING

Fortunately we can optimize $\dot{Q}_R$ without considering the parameter γ. Consider $\dot{Q}_R$ as introduced in Eq.(69a) and simplified in the symmetric case with $\mu = (\epsilon_1 + \epsilon_2)/2 = 0$ as in Eq.(75a).

$$\dot{Q}_r = \frac{\epsilon_2 - \epsilon_1}{2} (J_1 - J_2) = \epsilon (J_1 - J_2) \tag{85}$$

This equation takes into account all the same consideration and assumption that were made to obtain Eq.(84). However it is not analytically optimized. This is not a problem because Eq.(85) can easily be used to numerically optimize $\dot{Q}_R$ with respect to ϵ and ϵ_g as a function of T_R. In the strongly coupled system, where the energy-levels ϵ_1 and ϵ_2 are symmetric about the chemical potential ($\epsilon_2 = -\epsilon_1 = \epsilon \geqslant 0$), the levels of the quantum dots have to be adjusted continually according to keep the device operation within the window of refrigeration. Thus by

finding the values of ϵ and ϵ_g that maximize $\dot{Q}_R$, we also find its temperature dependence.

We performed the optimization using the C++ linear algebra library Armadillo [29], and the source code can be found in the appendix. In Fig.(15) we have plotted a surface map of $\dot{Q}_\tau$ as a function of ϵ and ϵ_g. In this scale the light shade represents cooling ($\dot{Q}_R > 0$), and dark shade heating ($\dot{Q}_R < 0$). The dotted lines marks the temperature $T_R = 50K$ at this instance, and the temperature of the cold left lead is $T_L = 100K$.

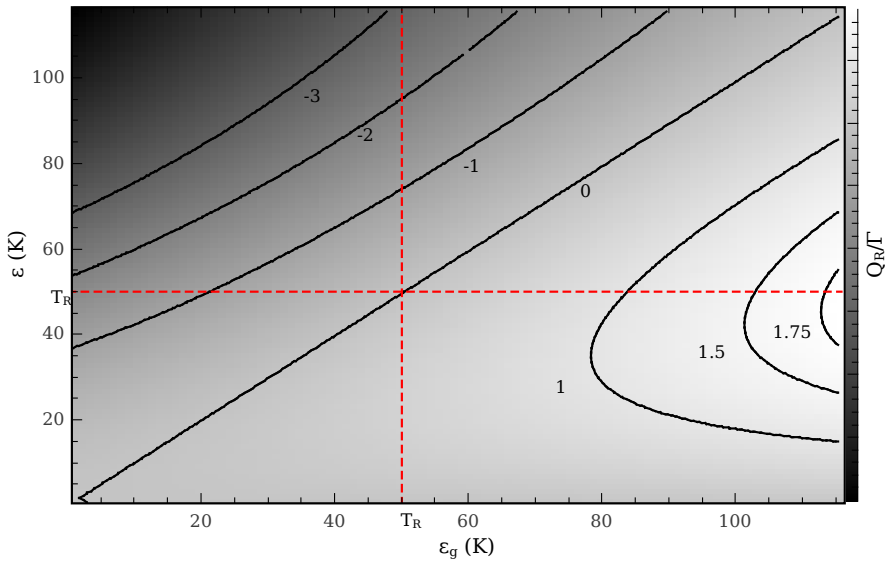

Figure 15: Surface plot of $\dot{Q}_R$ as a function of $\epsilon = \epsilon_2 = -\epsilon_1$ and ϵ_g. White represents cooling ($\dot{Q}_R > 0$) while black represents heating ($\dot{Q}_R < 0$). Here the cooling is maximized when ϵ is somewhere close to $T_R = 50K$ (which is marked by the red striped lines), and for large values of ϵ_g. For large values of $\epsilon_2 + \epsilon_g$ ($\epsilon_1 - \epsilon_g$) there is negligible current against the desired counter-clockwise direction due to the low(high) occupation in the Fermi-distribution far above(below) $\mu = 0$. Here $T_L = 100K$.

To analyze these results we need to consider behavior of the Fermi-distribution as a function of temperature. It immediately becomes clear that the optimal value of ϵ_g is very large. The high temperature of the Sun which drives the system can always produce a photon with enough energy to lift the electrons up an arbitrarily high energy difference relative to the energy scale of the system. When the energy level $\epsilon_2 + \epsilon_g$ is far above the chemical potential $\mu = 0$ the Fermi-distribution gives low

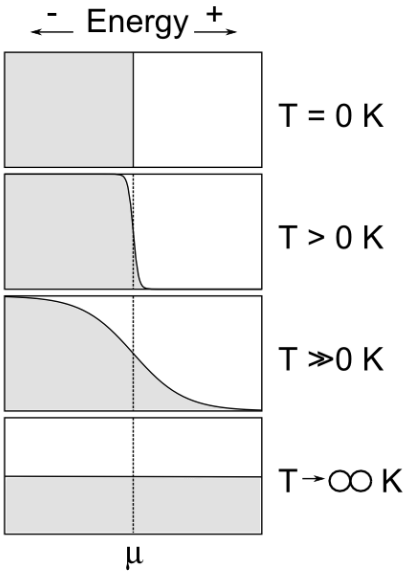

Figure 16: Schematic illustrating the Fermi-distributions temperature dependency. The shaded area represents occupied states, and there are always as many unoccupied states below μ as there are occupied states above.

occupancy. When there are no electrons occupying these high energy states there is no way for the electrons to move from the left lead into the quantum dot system, since it has to enter via the $\epsilon_2 + \epsilon_g$ level. A similar argument can be used for the energy level $\epsilon_1 - \epsilon_g$ far below the chemical potential, only here there is no way for the electron to move out of the quantum dot system into the right lead due to the high occupancy. Remember that we want to move cold electron out of the left lead and into the right lead (*condensation*), while moving hot electrons out of the right lead and into the left lead (*evaporation*). Thus we can remove any current against the desired counter-clockwise flow by choosing ϵ_g to be very large, as long as the energy can be provided by the heat-bath that preforms the work. In our case the Sun with a temperature of 5800 K is more than capable to provide photons with high enough energies to perform the work needed.

As for the optimized value of ϵ we see that it is somewhere slightly below the temperature $T_R = 50K$ marked with the dashed line. The optimized value of ϵ decreases linearly with T_R as the temperature is reduced. Again this can be understood by considering the shape of the Fermi-distribution. If ϵ is very large,

it would be far into the tail of the Fermi-distribution where the probability of transition is very low, resulting in a low particle current, but the energy transferred is high. On the other hand, if ϵ is very low, i.e. close to the chemical potential, the probability of transition is high, which results in a large particle current, but the energy transferred per transition $(\epsilon - \mu)$ would be very low. The natural intermediate position between these two extremes, is somewhere in the middle and linearly dependent on T_R. We can show by taking the derivative of $\dot{Q}_R$ with respect to ϵ_g and ϵ, and let $\epsilon_g/T_S \to 0$, that the value of ϵ that results in the maximum $\dot{Q}_R$ is given by

$$\epsilon^{max} = A\frac{T_R}{T_L}$$

where A is some constant.

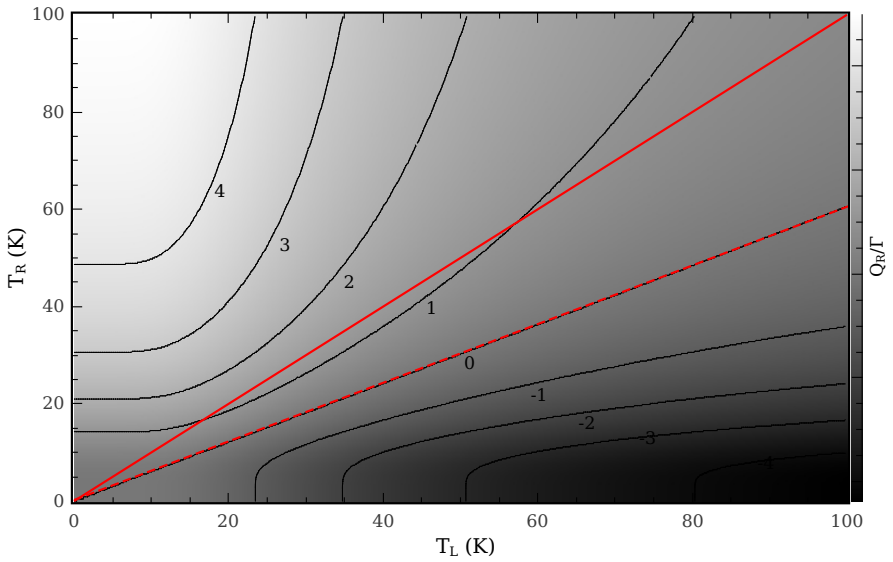

Figure 17: Surface plot of $\dot{Q}_R$ as a function of T_R and T_L. The dashed line traces the $T_R = T_L$ transition, thus for any point below it $T_R < T_L$ and for any point above it $T_R > T_L$. The zero heat-exchange contour-line lies in the area where $T_R < T_L$, and we can conclude that non-trivial cooling is possible in this system. The $T_R = T_L$ and zero heat-exchange line converges for low temperatures.

In Fig.(17) we display a surface plot of $\dot{Q}_R$ as a function of T_R and T_L, where again the white shade represents cooling while black represents heating. The dashed line is the line of temperature equilibrium, where $T_R = T_L$. For any point above this

line we have $T_R > T_L$. In this area the cooling is trivial and due to the natural flow of heat from hot objects to cold objects. However it is clear from the figure that there exists an area of cooling even for $T_R < T_L$, for the zero heat flow ($\dot{Q}_R = 0$) contour line lies below the dashed $T_R = T_L$ line. Any configuration of T_R and T_L between these two lines will result in non-trivial cooling. As the temperatures are reduced, zero heat-exchange and the $T_R = T_L$ lines converges.

We have shown that there exists optimized values of ϵ and ϵ_g which result in the highest possible cooling power $\dot{Q}_R^{max}$ by numerically analyzing the behavior of $\dot{Q}_R$ as a function of these parameters and finding a global maximum as shown in Fig.(15). From Fig.(17) we discover that this global maximum exists even when $T_R < T_L$, thus we can conclude that non-trivial cooling is a feature of the system, and that by continually keeping ϵ and ϵ_g in the global maximum configuration as a function of temperature the machine produces the maximal cooling power.

7.2 THE VERY LOW TEMPERATURE REGIME

Using what we have learned about the cooling machine in the previous section, we will now investigate what happens to the cooling power as we perform our optimization routine at very low temperatures. The source code for the optimization program can be found in the appendix. For each step in temperature we generate a matrix of $\dot{Q}_R(\epsilon, \epsilon_g)$ where the rows gives the ϵ value and the columns gives the ϵ_g value. Basically we generate a figure like the one in Fig.(15) for a discrete set of temperatures in an interval and maximize it. The procedure is summarized as follows:

1. Generate matrix of $\dot{Q}_R(\epsilon, \epsilon_g)$.
2. Find its maximal value.
3. Store $\dot{Q}_R^{max}(T_R)$, $\epsilon^{max}(T_R)$ and $\epsilon_g^{max}(T_R)$.
4. Change the temperature to $T_R + dT$ and repeat from step 1.

The end result of an optimization procedure is show in Fig.(18). Here $T_L = 25K$ for all the four plots, and we let T_R vary in an interval $T_R \in [0K, 50K]$. It is clear from (A) that as $T_R < T_L$ the maximized cooling power $\dot{Q}_R^{max}$ is highly suppressed when

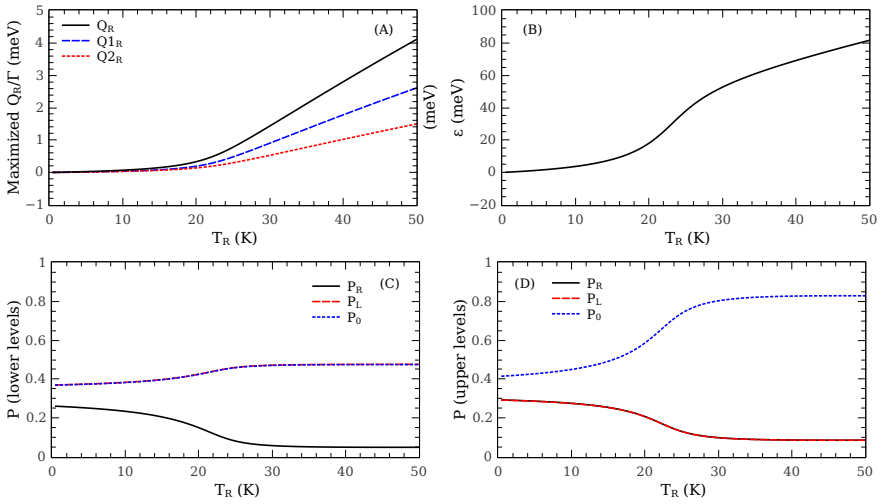

Figure 18: For the four plots in this figure the temperature $T_L = 25K$ and $\Gamma = \Gamma_s = 1$. (A) $\dot{Q}_R^{max}$ as a function of ϵ and ϵ_g where (B) is the value of ϵ which maximizes $\dot{Q}_R$, ϵ^{max}. The cooling power drops exponentially as the $T_R = T_L$ threshold is crossed. (C) and (D) shows the probabilities of occupying the states P_0, P_L, P_R for the lower (J_1) and the upper (J_2) levels respectively. These probabilities are relatively constant and only changes drastically during the transitions from $T_R > T_L$ to $T_R < T_L$.

compared to the $T_R > T_L$ region of trivial cooling. Nevertheless, there is still a non-zero flow of heat energy from the right lead, even when $T_R < T_L$. In (B) the value of ϵ that maximizes $\dot{Q}_R$ is shown. The occupation probabilities of the states P_0, P_L, P_R is shown in (C) and (D) for the set of lower and upper levels respectively. If we disregard the transition region from $T_R > T_L$ to $T_R < T_L$ the occupation probabilities changes little as a function of temperature. When we consider Eq.(85), this indicates that the leading contribution to the temperature dependence of $\dot{Q}_R$ at low temperatures comes from its proportionality to the energy ϵ, rather than to the net particle current $(J_1 - J_2)$. This corresponds well with the calculations of Cleuren et. al [5], where they found that $J_1 - J_2$ converges towards a small positive value in the limit of $T_R \to 0$.

$$\dot{Q}_r = \epsilon(J_1 - J_2)$$

When we decrease the temperature T_R to very low temperatures, we reach the linear regime as shown in Fig.(19). The optimized ϵ is linear as a function of T_R, and $\dot{Q}_R$ inherits this linearity due to the proportionality between them. The red

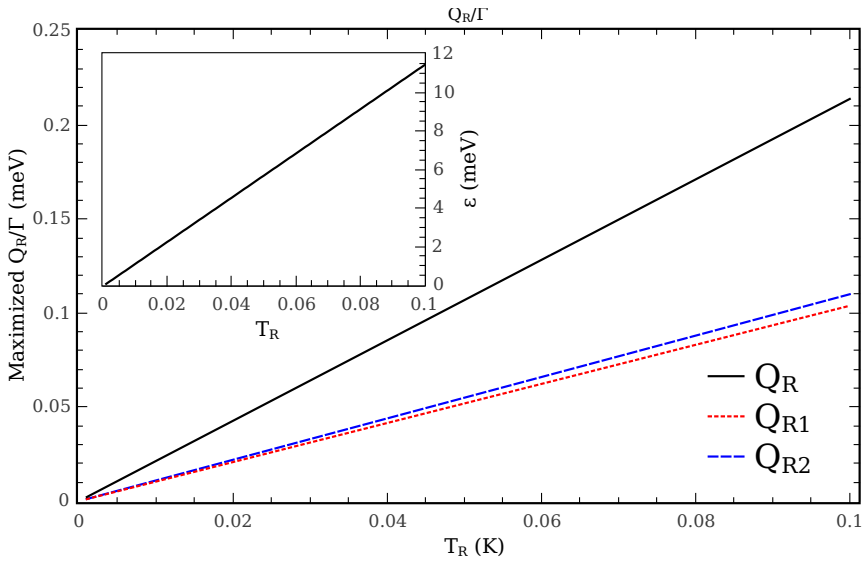

Figure 19: Plot of $\dot{Q}_R^{max}$ as a function of T_R for very low temperatures. In the regime where $T_R << T_L$ the cooling power scales linearly with T_R, just as predicted. The inset shows the value of ϵ which maximizes $\dot{Q}_R$ as a function of temperature.

dashed line in the plot is $\dot{Q}_R^1$ (heat-flux through the lower channel) while the blue one is $\dot{Q}_R^2$ (heat-flux through the upper channel). With this result we have numerically validated the claim of Cleuren et. al that $\dot{Q}_R \propto T_R$ as $T_R \to 0$.

In the next chapter we will propose a modification to the refrigerator model. We will argue that when we go to very low temperatures, the discrete quantum nature of the system has to be taken into account when calculating the cooling power and heat-capacity of the system, and that the fact that the authors neglected this is the primary reason why the third law is broken in their model. The third law is inherently statistical and quantum mechanical and by considering the discrete nature of metals at very low temperatures, we move away from the classical continuous description, and towards a real physical one.

8

FINITE ENERGY LEVEL SPACING

One of the assumptions of the model is that there is a continuous spectrum of energy states in the metal leads. Thus the electrons in the quantum dots is transferred elastically from its discrete state to the available state in the metal. And likewise in the metal-quantum dot transition. In real system however, there is a finite spacing between the energy levels in a metal. By replacing the continuous spectrum with a discrete one, we move the model one step closer to a real description of nature. In the Fermi-gas model of metals the energy levels are not evenly spaced as a function of energy. However in our model we will assume an even spacing since at the temperatures we are interested in $kT < \Delta$, where Δ is the spacing, all processes involving energy levels higher than the two lowest states is frozen out.

To evaluate whether this assumption has an effect on the cooling power at low temperature we introduce two new variables; δ, the asymmetry parameter and Δ, the energy-level spacing. In Fig.(20) a schematic of the discrete model is shown. Each energy-level in the right lead is separated by the gap Δ, and the asymmetry about the chemical potential μ is given by the parameter δ. When $\delta = \Delta/2$ the energy-levels are fully symmetric about μ, i.e. as you raise and lower ϵ_1 and ϵ_2 you cross the discrete levels in the metal lead simultaneously (since $\epsilon_1 = -\epsilon_2$).

When we now consider the transitions between the quantum dots and the metal lead, we realize that there are 2 possible transitions involving the level ϵ_1, as well as two transitions for the level ϵ_2. If we start counting the levels, and considering the first two levels above and below the chemical potential as the zeroth level, we see that the nth and mth level is characterized by the following energies:

- Above μ, the nth level (ϵ_2^*) is associated with the energy $\delta + n\Delta$.
- Below μ, the mth level (ϵ_1^*) is associated with the energy $\delta - (m+1)\Delta$.

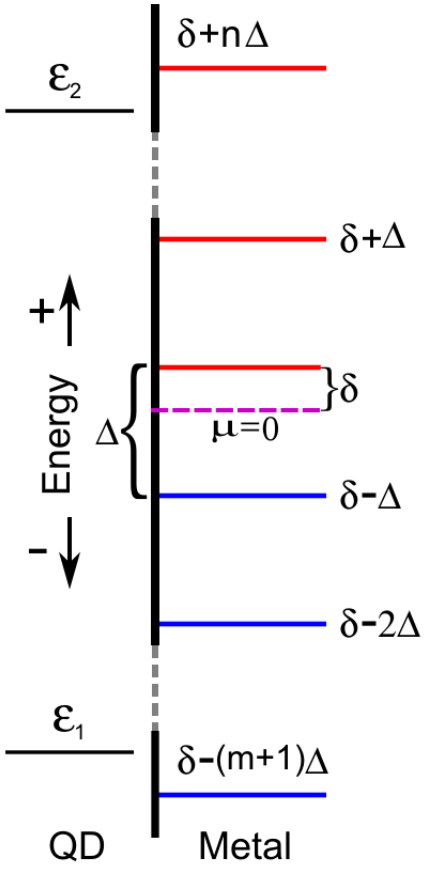

Figure 20: Schematic of the discrete model introduced in this section. The continuous states of the metal are replaced with a more realistic discrete spectrum by introducing a constant energy-gap, Δ, between each state. The asymmetry between states above/below the chemical potential is modeled by the parameter δ. For $\delta = \Delta/2$ the chemical potential lies exactly in the middle of two energy-levels and the energy-spectrum is symmetric.

In the discretized model, the energy transferred is not equal for transitions from and to the quantum dots and the metal. We consider only emission, which can be justified by making sure that the thermal energy kT is always smaller than the energy-level spacing Δ. For transition to take place between the levels, a phonon has to be emitted. Whether this phonon is then absorbed in the metal lead or dissipates into the substrate (imagine a large particle-bath surrounding both the system and the heat baths R and L) is crucial to determine the heat exchanged. In Fig.(21) and Fig.(22) all the possible transitions between the quantum dots and the metal are illustrated.

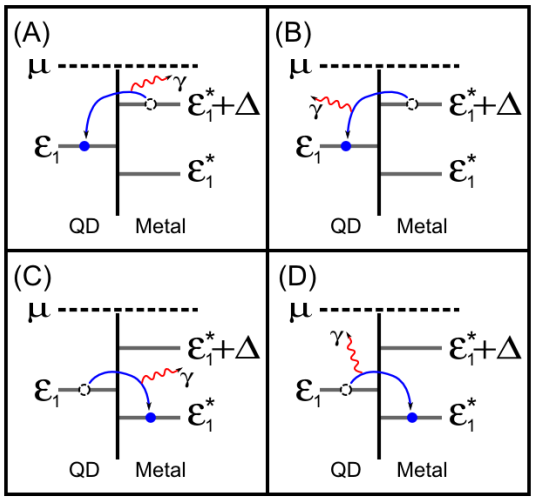

Figure 21: A schematic of all possible transitions between the energy level ϵ_1 and the right lead below the chemical potential. The red squiggly lines are phonon emissions and the blue straight lines are particle transfers. (A) and (C) shows the transitions metal→QD and QD→metal respectively, where the phonon is emitted in the lead. (B) and (D) shows the same transitions, only here the phonon is emitted in the substrate.

To correctly treat the discrete model we need consider where the phonon emitted during transitions is absorbed. The four possible transitions associated with the QD level ϵ_1 are summarized as follows:

(**A**) Phonon absorbed in lead before transition from lead to QD.
Heat transferred is $\Delta Q = \epsilon_1 - \mu < 0$.

(**B**) Phonon absorbed in substrate after transition from lead to QD.
Heat transferred is $\Delta Q = \epsilon_1^* + \Delta - \mu < 0$.

(**C**) Phonon absorbed in lead after transition from QD to lead.
Heat transferred is $\Delta Q = \epsilon_1 - \mu < 0$.

(**D**) Phonon absorbed in substrate after transition from QD to lead.
Heat transferred is $\Delta Q = \epsilon_1^* - \mu < 0$.

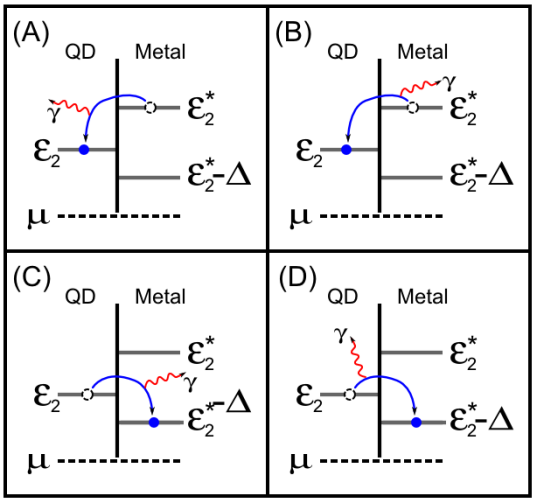

Figure 22: A schematic of all possible transitions between the energy level ϵ_2 and the right lead above the chemical potential. The red squiggly lines are phonon emissions and the blue straight lines are particle transfers. (A) and (B) shows transitions from the lead to the QD, where the phonon is emitted in the substrate and lead respectively. (C) and (D) shows the opposite transition form the QD to the lead, with the phonon emitted in the lead and substrate respectively.

And similarly, the transitions associated with the QD level ϵ_2, which is above the chemical potential, are summarized below.

(**A**) Phonon absorbed in substrate after transition from lead to QD.
Heat transferred is $\Delta Q = \epsilon_2^* - \mu > 0$.

(**B**) Phonon absorbed in lead before transition from lead to QD.
Heat transferred is $\Delta Q = \epsilon_2 - \mu > 0$.

(**C**) Phonon absorbed in lead after transition from QD to lead.
Heat transferred is $\Delta Q = \epsilon_2 - \mu > 0$.

(**D**) Phonon absorbed in substrate after transition from QD to lead.
Heat transferred is $\Delta Q = \epsilon_2^* - \Delta - \mu > 0$.

We must now redefine the heat flux, where we take into account the location of phonon emission/absorption. This is done by introducing the tuning-parameters α_1, α_2, β_1, $\beta_2 \in [0,1]$. Here α is related to transitions below the chemical potential, while β is associated with transitions above. The subscripts gives the path of the transition, where 1 is for the QD $\rightarrow$lead direction and 2 is for the lead$\rightarrow$ QD direction. The value of these parameters can be tuned between 0 and 1.

$$\begin{aligned}
\alpha_1, \alpha_2, \beta_1, \beta_2 = 1 &\quad \rightarrow \quad \text{Phonon absorbed in metal lead} \\
\alpha_1, \alpha_2, \beta_1, \beta_2 = 0 &\quad \rightarrow \quad \text{Phonon absorbed in substrate} \\
\alpha_1, \alpha_2, \beta_1, \beta_2 \in (0,1) &\quad \rightarrow \quad \text{Mixed absorption}
\end{aligned}$$

Now we can redefine the heat flux $\dot{Q}_R = \dot{Q}_{R_1} + \dot{Q}_{R_2}$, where $\dot{Q}_{R_1}$ is the heat flux through the lower channel, and $\dot{Q}_{R_2}$ the heat-flux through the upper channel, in the following form:

$$\begin{aligned}
\dot{Q}_{R_1} =& P_0^1 k_{l\to d}^{\epsilon_1^*+\Delta}\left[(\epsilon_1-\mu)\alpha_2 + (\epsilon_1^*+\Delta-\mu)(1-\alpha_2)\right] \\
&- P_R^1 k_{d\to l}^{\epsilon_1^*}\left[(\epsilon_1-\mu)\alpha_1 + (\epsilon_1^*-\mu)(1-\alpha_1)\right]
\end{aligned} \tag{86}$$

$$\begin{aligned}
\dot{Q}_{R_2} =& P_0^2 k_{l\to d}^{\epsilon_2^*}\left[(\epsilon_2-\mu)\beta_2 + (\epsilon_2^*-\mu)(1-\beta_2)\right] \\
&- P_R^2 k_{d\to l}^{\epsilon_2^*-\Delta}\left[(\epsilon_2-\mu)\beta_1 + (\epsilon_2^*-\Delta-\mu)(1-\beta_1)\right]
\end{aligned} \tag{87}$$

These equations accurately reflect the heat associated with each particle transfer, e.g. with $\alpha_1 = 0$ an electron moving from the QD level ϵ_1 to the metal lead level ϵ_1^*, brings with it the associated heat $\epsilon_1^* - \mu < 0$. The superscripts of the occupation probabilities P_0 and P_R are to separate the probabilities above and below the chemical potential in the same convention of the subscripts of $\dot{Q}_{R_1}$ and $\dot{Q}_{R_2}$.

After having clarified the heat exchange for each transition in the discrete model, we now need to consider the transition rates $k_{l\to d}$ and $k_{d\to l}$. These will not be the same as in the continuous version since they are functions of energy, which is no longer the same for the $l \to d$ and the $d \to l$ transitions. For the transition between ϵ_1 and the right metal lead, the new rates will be as shown in Eq.(88). Similarly, the transitions between ϵ_2 and the right lead results in the transition rates in Eq.(89).

$$\begin{aligned} k_{l\to d}(\epsilon_1^*) &= \Gamma f\left(\epsilon_1^* + \Delta\right) \\ k_{d\to l}(\epsilon_1^*) &= \Gamma\left[1 - f\left(\epsilon_1^*\right)\right] \\ \epsilon_1^* &= \delta - (m+1)\Delta \end{aligned} \tag{88}$$

$$\begin{aligned} k_{l\to d}(\epsilon_2^*) &= \Gamma f\left(\epsilon_2^*\right) \\ k_{d\to l}(\epsilon_2^*) &= \Gamma\left[1 - f\left(\epsilon_2^* - \Delta\right)\right] \\ \epsilon_2^* &= \delta + n\Delta \end{aligned} \tag{89}$$

We now have to redefine the master equation according to these transition rates, and calculate the new currents J_1^{dm} and J_2^{dm} for the discrete model. According to our model the master equation will now take the form shown in Eq.(90) for the lower channel, and Eq.(91) for the upper channel.

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 \\ k_{l\to d}^{\epsilon_1-\epsilon_g} & -k_{d\to l}^{\epsilon_1-\epsilon_g} - k_\uparrow & k_\downarrow \\ k_{l\to d}^{\epsilon_1^*+\Delta} & k_\uparrow & -k_{d\to l}^{\epsilon_1^*} - k_\downarrow \end{bmatrix} \begin{bmatrix} P_0^1 \\ P_L^1 \\ P_R^1 \end{bmatrix} \tag{90}$$

$$\begin{bmatrix} 1 \\ 0 \\ 0 \end{bmatrix} = \begin{bmatrix} 1 & 1 & 1 \\ k_{l\to d}^{\epsilon_2+\epsilon_g} & -k_{d\to l}^{\epsilon_2+\epsilon_g} - k_\downarrow & k_\uparrow \\ k_{l\to d}^{\epsilon_2^*} & k_\downarrow & -k_{d\to l}^{\epsilon_2^*-\Delta} - k_\uparrow \end{bmatrix} \begin{bmatrix} P_0^2 \\ P_L^2 \\ P_R^2 \end{bmatrix} \tag{91}$$

By finding the solutions of these stationary state master equations we obtain the occupation probabilities P_0, P_L, P_R for both the upper and lower channel. We can then define the particle currents via the same definition used earlier:

$$J_1^{dm} = P_R^1 k_{l\to d}^{\epsilon_1^*} - P_0^1 k_{l\to d}^{\epsilon_1^*+\Delta} \tag{92}$$

$$J_1^{dm} = P_R^2 k_{l\to d}^{\epsilon_2^*-\Delta} - P_0^2 k_{l\to d}^{\epsilon_2^*} \tag{93}$$

With these equations in hand, we can now calculate the thermodynamic properties of our discrete model, compare the results with the continuous model and investigate whether it obeys the third law of thermodynamics.

8.1 DEPENDENCY ON δ AND Δ

With the new discrete equations given in Eq.(86) and Eq.(87) we can use a similar C++ program to the one used for the continuous model. The source code for the numerical optimization of $\dot{Q}_R$ in the discrete model is given in the appendix. What follows in this section, is a discussion of the results obtained when analyzing the discrete model with this program.

We begin with Fig.(23), which shows the cooling power $\dot{Q}_R$ as a function of ϵ for the temperature indicated. The dotted lines are the data from the discrete model, while the continuous lines are from the original model. The temperature of the right lead is $T_R = 10K$ while the temperature of the left lead $T_L = 25K$. Due to the discrete nature of the model, the cooling power $\dot{Q}_R$ experience stepwise variations as a function of ϵ. These steps represents the crossing of ϵ_1/ϵ_2 with the energy levels of the metallic lead. In the case of Fig.(23) the asymmetry parameter is $\delta = \Delta/2$, therefore both ϵ_1 and ϵ_2 cross the levels in the metal at the same time, resulting in a simultaneous change of $\dot{Q}_{R_1}$ (blue) and $\dot{Q}_{R_2}$ (red). The maximal cooling power is found to be slightly higher, and shifted towards $\epsilon = 0$ in the discrete case relative to the continuous. As we decrease the spacing between the energy-levels of the metal lead we expect the results from the discrete model to converge to that of the continuous model since any low-energy features will be wiped out by the thermal energy when kT exceeds the characteristic energy (Δ in this case). Our assumption is confirmed by Fig.(24), where we see the data from the discrete model (dots) converge with the data from the continuous case (lines).

An alternate scenario is shown in Fig.(25), where $\delta = \Delta/4$ which results in an asymmetric crossing of the QD levels and the levels of the metallic lead. This asymmetry is illustrated by the vertical black(red) lines that shows that while $\epsilon_1(\epsilon_2)$ is within the gap between two energy-levels, $\epsilon_2(\epsilon_1)$ crosses a level above(below) the chemical potential. The result is that the total cooling power $\dot{Q}_R$ varies in discrete steps, with widths of alternating size.

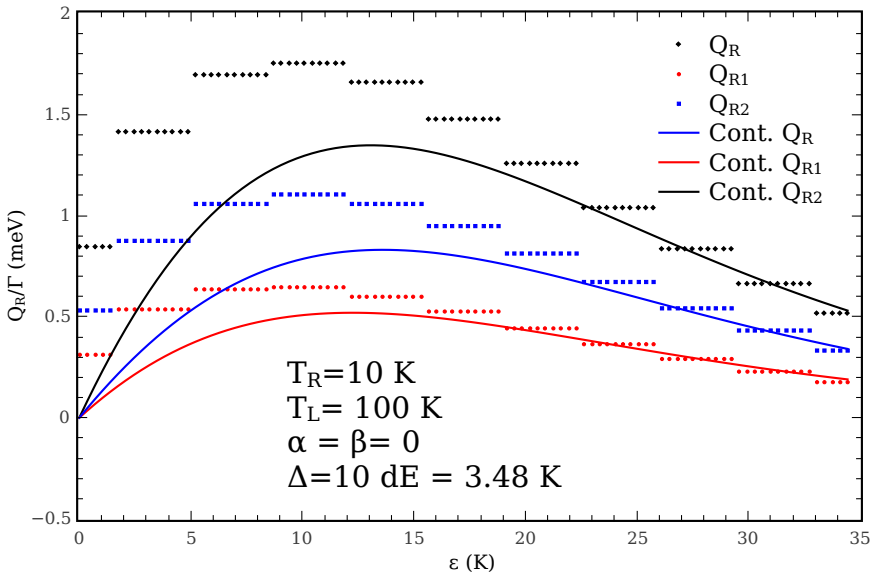

Figure 23: Graph of $\dot{Q}_R$ as a function of ϵ for $T_R = 10K$ and $T_L = 100K$, with a level spacing $\Delta = 3.5K$. The dotted lines are data from the discrete model, while the continuous lines are from the original model. We observe a finite difference between the two models for lower temperatures, with the cooling power being higher in the discrete case.

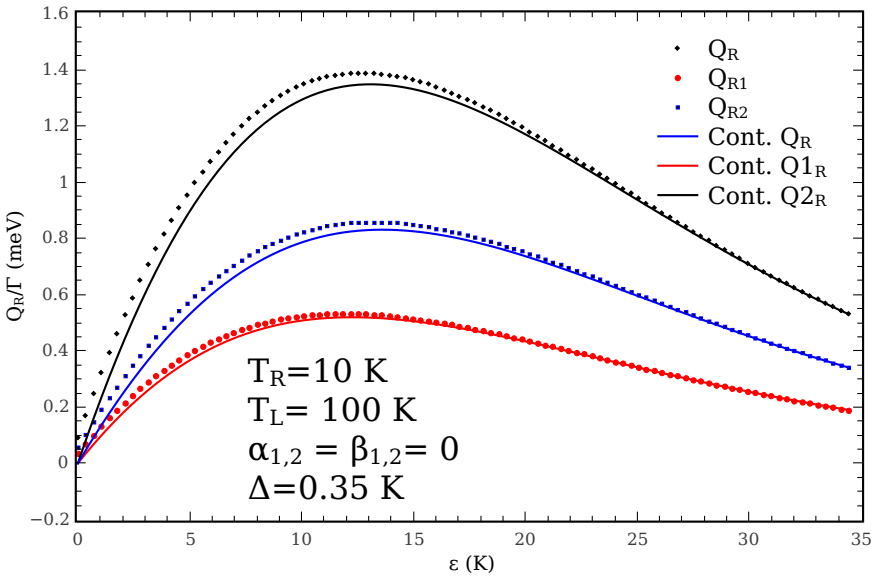

Figure 24: Graph of the $\dot{Q}_R$ as a function of ϵ for small spacing between the energy levels of the metal lead, $\Delta = 0.35K$. The dots are data from the discrete model, while the lines are from the continuous model. We expect the discrete model to converge to the continuous model when $\Delta < kT$, due to the thermal smearing of low-energy details.

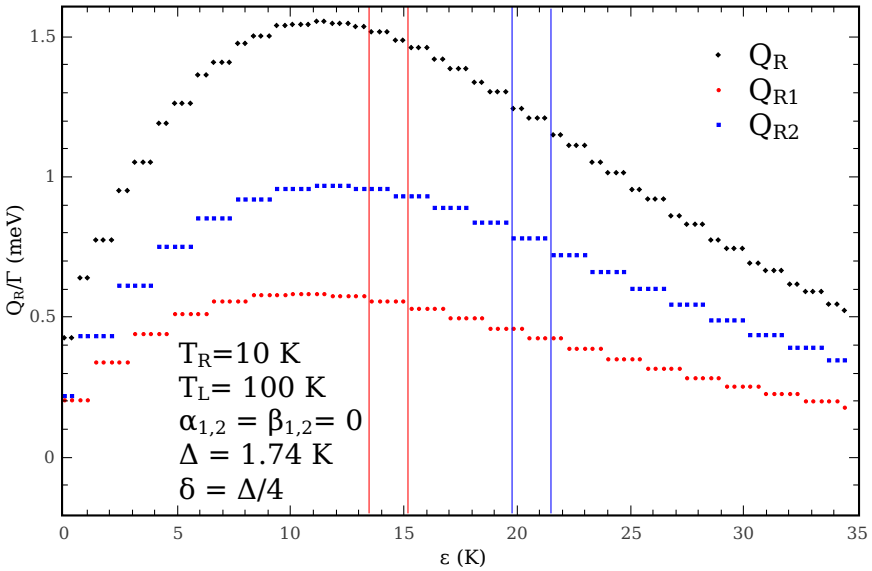

Figure 25: Graph of $\dot{Q}_R$ as a function of ϵ with an asymmetry-parameter $\delta = \Delta/4$. Since $\dot{Q}_R = \dot{Q}_{R_1} + \dot{Q}_{R_2}$, and $\dot{Q}_{R_1}$ is shifted relative to $\dot{Q}_{R_2}$, the cooling power experiences a odd-even stepsize alternation. The vertical red(black) lines shows how the alternating stepsize arise from the asymmetry about the chemical potential.

8.2 MAXIMIZED COOLING POWER

For simplicity we set $\delta = \Delta/2$ in the following discussion, and we will later show that the results obtained in this section will be valid for any value of δ. In Fig.(26) we show the results from performing the optimization of the discrete model. For small values of Δ (black line) the results are, as expected, similar to those obtained by the continuous model, i.e. the cooling power scales linearly with T_R. However, as we increase Δ we observe a new feature appear for very-low temperatures ($T_R > 0.2$K). The cooling power quickly drops in a non-linear fashion. With higher values of Δ this feature appears at higher temperatures, but it is clear that the feature exists for all the plots in Fig.(26). With higher resolution we would be able to observe a similar behavior for the apparently linear black line.

By increasing the energy-spacing Δ to enhance the low temperature details, we obtain the graph shown in Fig.(27). Here the straight green line is the data from the continuous model, while the red, blue and black line was obtained by $\alpha_1 = \alpha_2 = \beta_1 = \beta_2 = 0$, 0.5 and 1 respectively. This corresponds to full

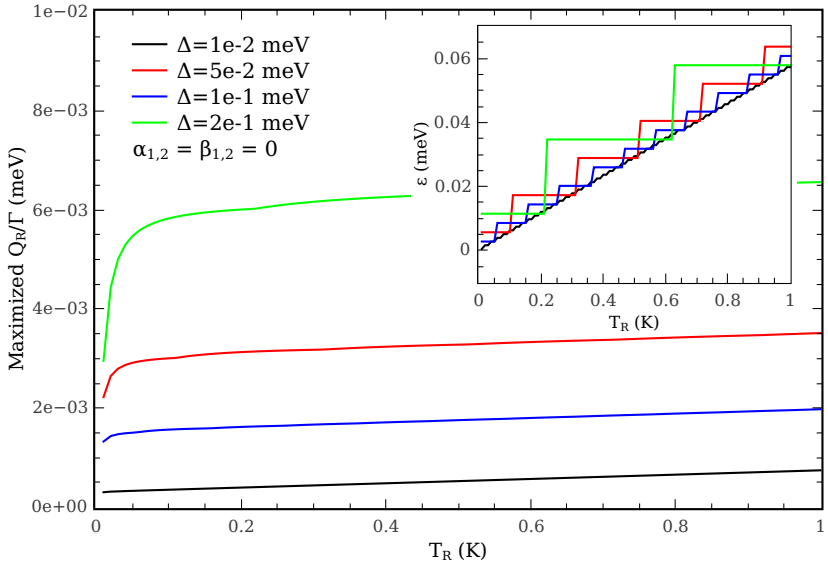

Figure 26: Graph of the optimized cooling power $\dot{Q}_R$ as a function of temperature T_R for the discrete model with varied values of Δ. For small values of Δ (black line) the results are approximately the same as for the original model, i.e. $\dot{Q}_R \propto T_R$. As we increase Δ a new feature appears in the very-low temperature regime with non-linear behavior. The inset graph shows the value of ϵ that maximizes $\dot{Q}_R$ for each value of Δ.

phonon absorption in the substrate (0), mixed absorption (0.5) and full absorption in the metal lead (1). The end result is a clear deviation from the linear behavior of the continuous model, regardless of where the phonon are absorbed. It is worth noting that this non-linear decay of cooling power happens all within the final energy level, i.e. between the δ and $\delta - \Delta$ level above and below the chemical potential respectively.

We now need to find out how the cooling power curves from the discrete model shown in Fig.(27) scales as a function of temperature. Does it scale as a power law, an exponential or something in-between? By graphically representing the data in four ways shown in Fig.(28), it is easy find the behavior of $\dot{Q}_R$ at low temperatures. First, in (A) we show the raw data of cooling power versus temperature, which is just the same as in Fig.(27). The plots (C) and (D) shows two ways to look for power law behavior. If the cooling power is proportional to some power of the temperature we obtain

$$\dot{Q}_R = AT^x$$

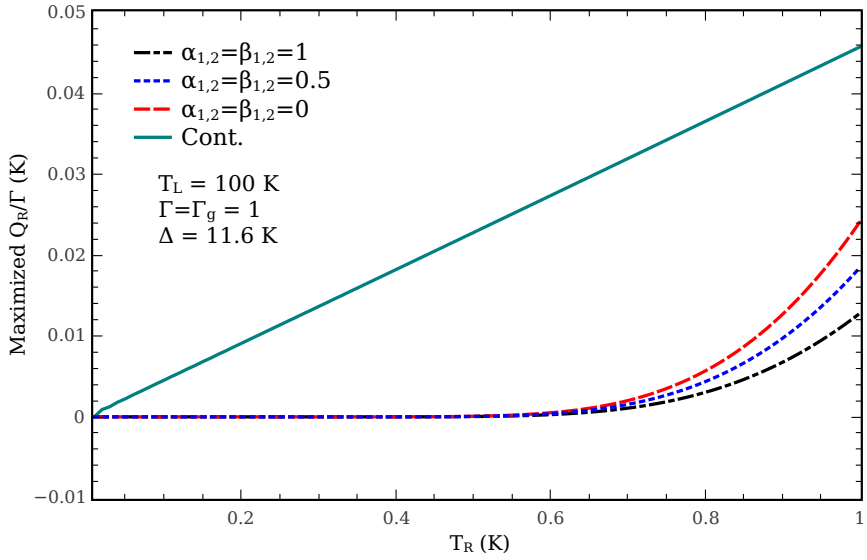

Figure 27: Graph of the cooling power $\dot{Q}_R$ at very low temperatures made from results obtained by the discrete model, compared with the result from the continuous model (green line).

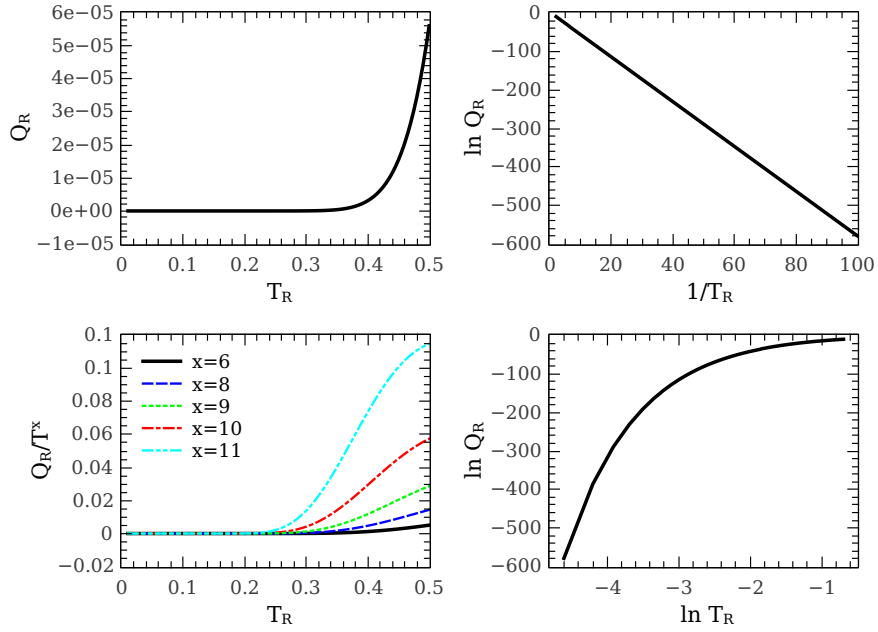

Figure 28: Four different ways to display the maximized cooling power as a function of temperature. (A) is a linear plot, (B) is an Arrhenius plot, (C) and (D) are two examples of power law plots. It is evident from the linearity of (B) that $\dot{Q}_R$ is an exponential function of T_R at low temperatures.

$\alpha_{1,2} = \beta_{1,2}$	A	σ A	B	σ B
0	1.992	2.712e-2	−5.811	1.693e-3
0.5	1.737	2.371e-2	−5.810	1.481e-3
1	1.393	1.393e-2	−5.807	1.120e-3

Table 1: Here we show the fitting parameters from the Arrhenius equation $\dot{Q}_R = A\exp(B/T)$, as well as their uncertainties, for various values of $\alpha_{1,2}$ and $\beta_{1,2}$.

and to find the power, x, one can try plotting $\dot{Q}_R/T^x$ for various trial-values of x as in (C) to look for value that returns a straight line.

$$\dot{Q}_R/T^x = A$$

Or one can simply show the data in a log-log plot as in (D), where we expect a straight line with a slope that equates to the power x according to the equation

$$\ln\dot{Q}_R = \ln A + x\ln T$$

We realize that neither (C) nor (D) shows any of the characteristic expected of a power law function. This leads to the graph shown in (B), which represents the data as the logarithm of $\dot{Q}_R$ versus the inverse temperature and is known as an Arrhenius plot. If $\dot{Q}_R$ is an exponential function we have

$$\dot{Q}_R = A\exp(B/T)$$

and by taking the logarithm on both sides we obtain

$$\ln\dot{Q}_R = \ln A + \frac{B}{T}$$

which corresponds to a straight line if we plot $\ln\dot{Q}_R$ versus $1/T$. Thus it is evident from (B) that the cooling power is an Arrhenius function.

We set the asymmetry-parameter $\delta = \Delta/2$, i.e. we were considering the case where the energy levels symmetrically distributed relative to the chemical potential. By calculating the optimized $\dot{Q}_R$ as a function of temperature and fitting the data to the Arrhenius function, we obtained the parameters as shown

in Table 1. We used an energy spacing of $\Delta = 1\ meV = 11.6$ K, and thus we recognize that the fitting parameter B is equal to $\Delta/2 = \delta$. We conclude thus that the cooling power $\dot{Q}_R$ depends exponentially on temperature in the limit of $T_R \to 0$, and has the following form:

$$\lim_{T_R \to 0} \dot{Q}_R \propto e^{-\frac{\Delta/2}{T_R}} \tag{94}$$

Although this analysis is only valid for $\delta = \Delta/2$, we will show later that similar results is obtained for $\delta \in [0, \Delta]$.

8.3 HIGHER ORDER TRANSITIONS

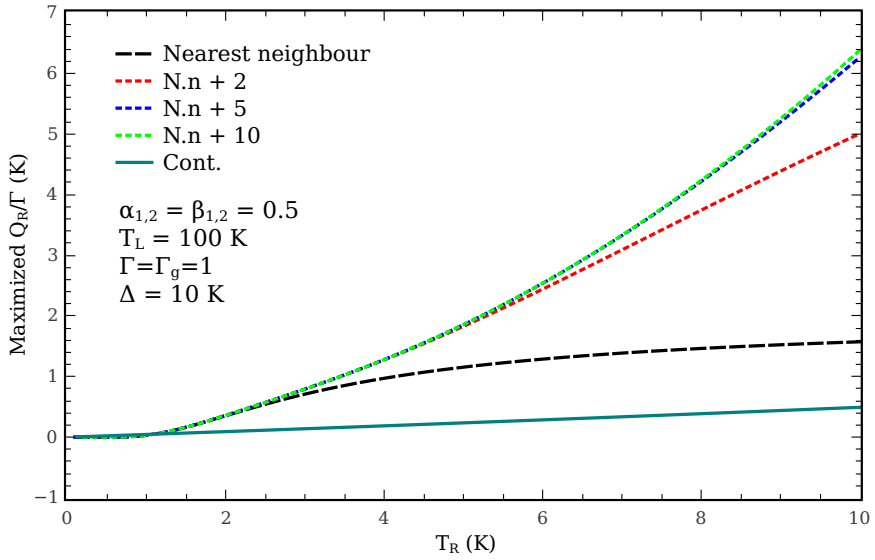

Figure 29: Here we show the results obtained by including higher order transitions into the model, compared to the continuous model and the neighboring-level transition model. The increase in cooling power due to higher order transitions is considerable at high temperatures, however this effect vanishes at lower temperatures (below 2 K) where the cooling power is virtually independent of how many levels one include.

So far we have only considered electron transitions from(to) the energy levels of the metal lead directly above(below) the quantum dot level ϵ_1/ϵ_2. By extending the model to include higher order transitions we obtained the results shown in Fig.(29). The cyan continuous line is the data from the continuous model, the black dashed line is from the discreet model with only tran-

sitions between nearest neighbor levels are taking into consideration, whereas the dotted lines (red, blue, green) are where we include higher order transitions (2, 5 and 10 next-nearest neighbors).

At high temperatures the increase in maximized cooling power due to additional available transitions is considerable. However this additional increase in cooling power gained by including transitions from higher energy levels dies of quickly, as can be seen in the small difference between the 5 and 10 next-nearest neighbor curves. As the temperature is lowered all the curves converges to the model with only nearest neighbor transitions. Any transitions other than the nearest neighbor transition is quenched when $kT << \Delta$ since the Fermi occupation probability for the states of higher energy goes exponentially to zero. This indicates that in the limit of $T_R \to 0$, we only need to consider the final energy levels above and below the chemical potential.

8.4 HEAT CAPACITY OF THE DISCRETE MODEL

With the introduction of the discrete energy-spectrum we can no longer claim that the heat capacity is linearly proportional to T as $T \to 0$.

$$C \propto T$$

This is a result obtained from the free electron Fermi gas-model of metals, which is only valid in the case of a continuous energy-spectrum. For the derivation of the heat capacity of a Fermi-gas in the continuous energy distribution approximation, see Kittels "Thermal Physics" [13] or an equivalent textbook on statistical thermodynamics. The result is given by

$$C = \frac{dU}{dT} = \int_0^\infty d\epsilon \big(\epsilon - \mu\big) D(\epsilon) \frac{df(\epsilon)}{dT} \tag{95}$$

Where $D(\epsilon)$ is the density of states, $f(\epsilon)$ is the Fermi-distribution, and ϵ_F is the Fermi-energy. The Fermi-energy is defined as the chemical potential at $T = 0$ K, and thus at absolute zero all states below ϵ_F are occupied while all above are unoccupied. By integrating this equation, and taking the limit as $T \to 0$, one finds that $C \propto T$.

When going from the continuous to the discrete description we have to exchange the integral with a sum, and the discrete energy ϵ with the quantized energy levels $i\Delta$, where i is a integer number.

$$C = \sum_{i=1}^{\infty} (i\Delta - \mu)^2 \frac{1}{T^2} \frac{e^{(i\Delta-\mu)/T}}{(e^{(i\Delta-\mu)/T} + 1)^2} \tag{96}$$

This sum can be solved numerically. Again we have set $\delta = \Delta/2$ for simplicity. By fitting the data to a function on the form

$$C = \frac{A}{T^B} e^{-D/T}$$

where A,B and D are fitting parameters, we obtain an exact expression for the heat capacity for the case where $\delta = \Delta/2$, in the limit of $T_R \to 0$.

$$C = \frac{2(\Delta/2)^2}{T^2} e^{-\frac{\Delta/2}{T}} \tag{97}$$

We recognize that the exponential term $e^{-\frac{\Delta/2}{T}}$, as the exact same we obtained for the cooling power $\dot{Q}_R$.

Although we could not find an analytical expression for the heat capacity for all temperatures, we can find one for $T \to 0$. Consider the two energy levels δ and $\delta - \Delta$, which are the only possible states the electrons can occupy in the limit of $T \to 0$. The grand canonical partition function for this system is given by

$$Z = \sum_i e^{-\beta H_i} = 1 + e^{-\beta(\delta)} + e^{-\beta(\delta-\Delta)} + e^{-\beta(2\delta-\Delta)} \tag{98}$$

Here H_i is the full Hamiltonian of state i. There are four possible states of the system, if we allow for a varying number of electrons, which we must in an open system.

1. $H_0 = 0$, no electron occupying either state.
2. $H_1 = \delta$, one electron occupying the δ state.
3. $H_2 = \delta - \Delta$, one electron occupying the $\delta - \Delta$ state.
4. $H_3 = 2\delta - \Delta$, one electron occupying the δ state, and one electron occupying the $\delta - \Delta$ state.

The energy of this two level system is given by

$$U = \frac{\sum_i H_i e^{-\beta H_i}}{Z}$$

$$U = \frac{\delta e^{-\beta(\delta)} + (\delta - \Delta)e^{-\beta(\delta-\Delta)} + (2\delta - \Delta)e^{-\beta(2\delta-\Delta)}}{1 + e^{-\beta(\delta)} + e^{-\beta(\delta-\Delta)} + e^{-\beta(2\delta-\Delta)}} \tag{99}$$

And we can then calculate the heat capacity using

$$C = \frac{dU}{dT} = -\frac{1}{T^2}\frac{dU}{d\beta} \tag{100}$$

$$\begin{aligned} C = \; - \; & \frac{1}{T^2}\Bigg[\frac{\Delta^2\left(e^{\beta(\Delta-3\delta)} + e^{\beta(\Delta-\delta)} + 2e^{\beta(\Delta-2\delta)}\right)}{\left(1 + e^{-\beta(\delta)} + e^{-\beta(\delta-\Delta)} + e^{-\beta(2\delta-\Delta)}\right)^2} \\ & + \frac{\delta^2\left(e^{\beta(\Delta-3\delta)} + e^{\beta(2\Delta-3\delta)} + e^{\beta(\Delta-\delta)} + 4e^{\beta(\Delta-2\delta)} + e^{-\beta\delta}\right)}{\left(1 + e^{-\beta(\delta)} + e^{-\beta(\delta-\Delta)} + e^{-\beta(2\delta-\Delta)}\right)^2} \\ & + \frac{\Delta\delta\left(2e^{\beta(\Delta-3\delta)} + 2e^{\beta(\Delta-\delta)} + 4e^{\beta(\Delta-2\delta)}\right)}{\left(1 + e^{-\beta(\delta)} + e^{-\beta(\delta-\Delta)} + e^{-\beta(2\delta-\Delta)}\right)^2}\Bigg] \end{aligned} \tag{101}$$

As you can see, the general solution is large and messy. It is however important to notice that it is a product of the factor $1/T^2$, and massive sum of exponential functions. Finally, the equation is greatly simplified by setting $\delta = \Delta/2$. By doing this we obtain

$$C = \frac{2(\Delta/2)^2}{T^2}\frac{e^{\beta\Delta/2}}{(e^{\beta\Delta/2} + 1)^2} \tag{102}$$

and if we now take the limit as $T \to 0$ (or equivalently $\beta = 1/T \to \infty$) the term $e^{\beta\Delta/2}$ becomes much larger than 1, and thus we can safely ignore the 1 in the denominator to obtain

$$\lim_{T\to 0} C = \frac{2(\Delta/2)^2}{T^2}\frac{e^{\frac{\Delta/2}{T}}}{e^{\frac{\Delta}{T}}} = \frac{2(\Delta/2)^2}{T^2}e^{\frac{-\Delta/2}{T}} \tag{103}$$

We recognize that this analytically derived result is the same as we found numerically in Eq.(97).

8.5 THE UNATTAINABILITY OF ABSOLUTE ZERO

Now it is time investigate whether the third law is obeyed in our discretized model. With the results obtained in the previous sections we expect to find

$$\lim_{T_R\to 0}\frac{dT}{dt} = \lim_{T_R\to 0}\frac{\dot{Q}_R}{C} \propto \frac{e^{-\frac{\Delta/2}{T_R}}}{T_R^{-2}e^{-\frac{\Delta/2}{T_R}}} = T_R^2$$

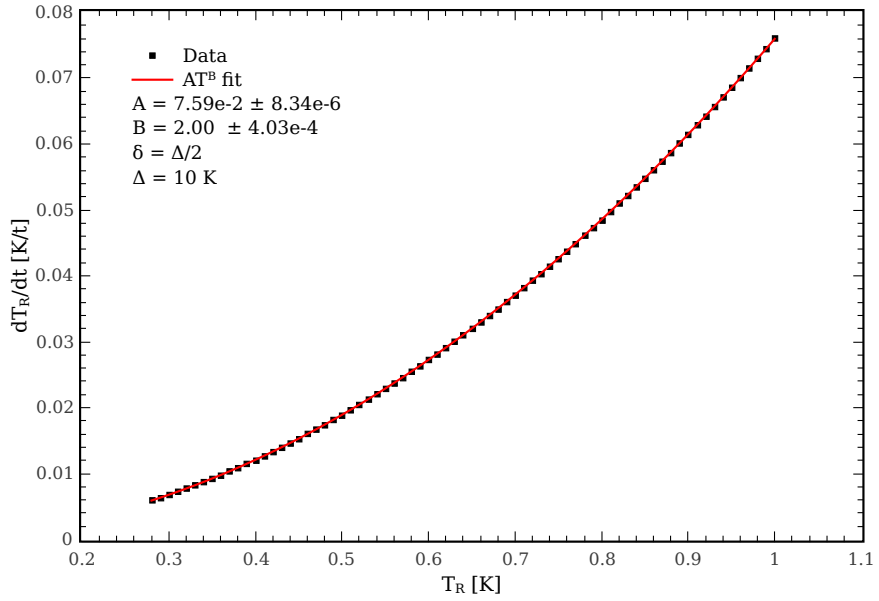

Figure 30: Plot of dT_R/dt as a function of T_R in the limit of $T_R \to 0$. Here we consider the case where $\delta = \Delta/2$. The data is shown as black squares, while the red line is the fit to a function of the form $A\ T^B$. We see that the exponential terms of $\dot{Q}_R$ and C cancel, and we are left with $dT_R/dt \propto T^2$.

In Fig.(30) we have plotted $dT_R/dt = \dot{Q}_R/C$ as a function of temperature, and indeed we verify that dT_R/dt is proportional to T_R^2 as $T_R \to 0$. We discussed earlier that according to Eq.(18), the unattainability principle requires that if dT/dt has the following form

$$\frac{dT_R}{dt} \propto T^\alpha$$

the exponent α has to be larger than 1. In the continuous energy distribution model as introduced by Cleuren et al. it was found that $\alpha < 1$. However now that we have considered the discrete distribution of the energy levels we find that $\alpha = 2 > 1$, and thus the third law of thermodynamics is not violated.

These results are, as mentioned, only valid for $\delta = \Delta/2$. As seen in Eq.(101) the heat capacity as a function of δ is a large and complicated function. And since we do not have a general expression for $\dot{Q}_R$, the final test of whether the third law is obeyed in our system for all values of δ has to be numerical. Intuitively it makes sense that when the third law is obeyed for one value of δ, it is obeyed for all values. Nothing is fundamen-

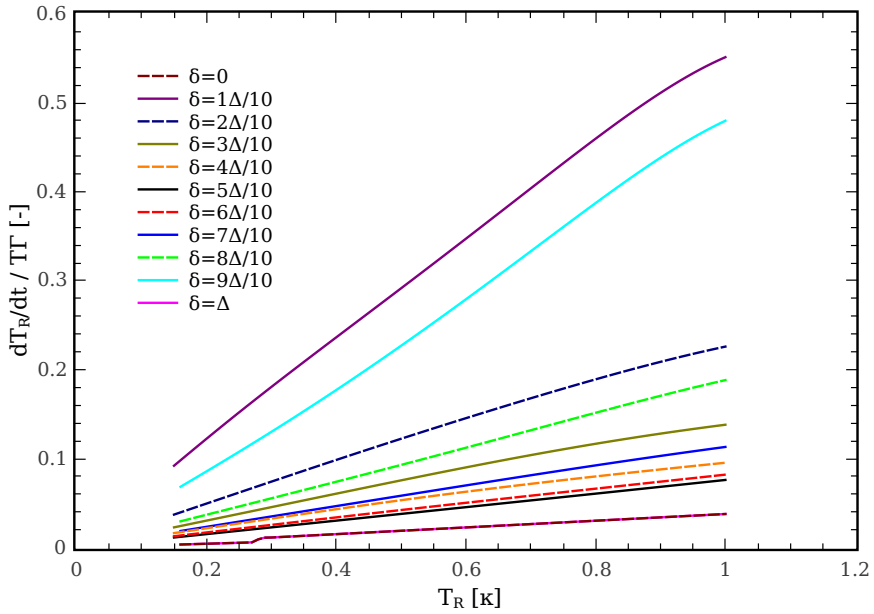

Figure 31: Plot of $\frac{dT_R}{dt}\frac{1}{T_R}$ as a function of T_R for multiple values of $\delta \in [0, \Delta]$. We see that regardless of the value of δ chosen, all the lines converge towards 0, in accordance with the third law of thermodynamics.

tally changed in the system when the chemical potential moves away from the center. Nevertheless, to verify our assumption we calculated $\frac{dT}{dt}$ for several values of δ. An equivalent statement of saying that α has to be larger than one, is that

$$\frac{dT_R}{dt}\frac{1}{T_R} \propto T_R^{\alpha-1} \tag{104}$$

has to converge to 0 as $T_R \to 0$. This equation diverges if $\alpha < 1$ and in the limiting case of $\alpha = 1$ it goes towards a constant value. In Fig.(31) we have plotted $\frac{dT_R}{dt}\frac{1}{T_R}$ as a function of T_R for multiple values of δ. We see that $\frac{dT_R}{dt}\frac{1}{T_R} \to 0$ as $T_R \to 0$, just as demanded by the third law, and thus we conclude that the unattainability principle is upheld in our discrete model regardless of the value we choose for δ.

9 CONCLUSION

In this final chapter we will summarize the work that we have done and what results we have obtained in this master thesis. We will then discuss our findings as well as give recommendations for further extensions for the work.

9.1 SUMMARY AND CONCLUSIONS

This master thesis have been an investigation into the application of the third law of thermodynamics. We have considered a nano-refrigerator system presented by other authors, that generated much discussion within the community due to its apparent violation of the unattainability formulation of the third law; one can not cool a system to absolute zero in a finite amount of time. Our main objective was to find out why the third law was violated in this model and how we could modify it, with the least amount of change in the assumptions made by the original authors, to the point where the third law was upheld. In our opinion none of the proposed solutions made in the discussion surrounding the model was satisfactory. They either consisted of analyzing similar models and drawing conclusions from those, or by pointing out flaws that easily could be rectified with small modifications. None of them suggested explicit solutions, and we felt that this was a problem that needed to be solved.

In the first three chapters of this master thesis we have introduced key thermodynamical concepts needed to understand the operation of the cooling system. Since the laws of thermodynamics are closely connected to the concept of entropy, we described in detail how to interpret this sometimes confusing topic in Chapter 1, where we also presented the first three laws of thermodynamics to create a smooth transition into the third law. We then introduced in Chapter 2 the third law in its various incarnations; first as the heat theorem which concerns the vanishing entropy difference at absolute zero, then in the form of the unattainability principle which was shown to be a direct consequence of the heat theorem. Following this we dis-

cussed in Chapter 3 what would qualify as a violation of the laws of thermodynamics. In Chapter 4 we introduced the refrigerator model as the main topic of the thesis, showed how it violates the third law, and summarized the discussion of that followed due to this violation. In the discussion multiple solutions was proposed, and in this chapter we also explained why we found them unsatisfactory. Then, in Chapter 5 we presented the theoretical framework of stochastic thermodynamics, which is used to describe out-of-equilibrium systems, and needed to understand the function of the refrigerator. Following this we used those theories explicitly in Chapter 6 to analytically describe the thermodynamic properties of the refrigerator model. Here we showed, by following the assumptions and calculations made by the original authors, that the cooling power of the refrigerator scales linearly as a function of temperature in the low temperature limit, which is a behavior prohibited by the third law. In Chapter 7 we analyzed the model numerically check whether the cooling power really had this violating form, since we found the final steps made in the mathematical derivation by the original authors unconvincing. Our numerical results confirmed the behavior of the analytically derived cooling power. Finally in Chapter 8 we introduced a refinement of the original model. We considered the fact that the there is a discrete spacing between energy levels in a metal, and at low temperatures we can no longer consider the energy distribution continuous. We found that with this consideration the third law of thermodynamics was restored.

9.2 DISCUSSION

Even though the third law of thermodynamics is over 100 years old there is still confusion about how to interpret what constitutes a violation of it. Thermodynamics is in essence the science of energy-transformations, and its statements and theories are so general that they are considered independent of the description of the system under investigation. The third law is a theory about what happens to a system as its temperature approaches absolute zero, and at these low temperatures nature is described by quantum mechanics. Quantum mechanics predicts that all systems has discrete energy levels, and when the heat energy kT becomes comparable to the energy difference Δ between these discrete levels this discreteness needs to be taken into consideration. Therefore the third law has to be con-

sidered an exception to the general validity of the theories of thermodynamics. It is an intrinsically quantum mechanical theory, and it can not be used to make any claims about classical systems. This is an exceptional realization when considering that the third law in its first incarnation, the Nernst heat theorem, was formulated before quantum theory.

In our analysis of the refrigerator model we have found that the third law is violated because in the original description the metal lead that is cooled is considered to have a continuous energy-spectrum which we can not assume when the temperature approaches absolute zero. When the metal, which is considered a Fermi-gas, approaches absolute zero the energy distribution is in reality discrete. By taking into consideration this discrete energy distribution we have refined the model into a quantum mechanical one, and we have shown that the third law is no longer violated. We conclude that the model as originally proposed is valid until we reach temperatures $kT \approx \Delta$.

9.3 RECOMMENDATIONS FOR FURTHER WORK

In order to some day create a real quantum refrigerator from the model presented in this thesis one needs to consider the fact that the metal lead will be charged when the chemical potential $\mu = 0$. It is therefore beneficial to find out how the refrigerator behaves when we let the chemical potential of the right and left lead be non-equal, such that we can a net particle current $J_1 + J_2 = 0$ which prevents charging. Also if one really want to push the limit of cooling towards absolute zero in a real system, one needs to take into account quantum effects that become pronounced at these temperatures. A future study of the model could investigate what happens to the cooling power when one for example considers different models of the electron-phonon interaction.

In Fig.(31) we see that the value chosen for δ affects the cooling rate. With further analysis we could find the cooling rate as a function of δ, to see which value gives the maximal cooling rate.

We have assumed that the right lead equilibrates instantaneously during electron transfer. But this equilibration depends on the size of the metal. Larger volumes takes longer time to

equilibrate, and the cooling would only happen in a finite area of the metal. Not only does the size affect the equilibration time, but it also affects the spacing between the energy levels. Larger volumes gives smaller spacing, and thus the model proposed could cool to lower temperatures since the cooling rate vanish only when $kT \sim \Delta$. Further study to investigate the optimal volume versus cooling rate would be beneficial.

Finally we have assumed that the left lead function as a large heat bath, and have no effect on the cooling rate. A recent article have shown that in a cooling process the density of states of the heat bath affects the cooling rate of quantum refrigerators [20]. A refined model where we take into account the properties of the left lead heat bath would give us additional insight into the nature of quantum refrigerators.

APPENDIX

A.1 C++ SOURCE CODE FOR THE CONTINUOUS MODEL

```
#include <iostream>
#include <math.h>
#include <time.h>
#include <fstream>
#include <iomanip>
#include <armadillo>


using namespace arma;
using namespace std;


//-----------------------------------------//
// P0, Pl and Pr for the lower levels.
//-----------------------------------------//

double P0_1 (double Ts,double Tr,double Tl, double gamma_s,
double gamma, double Eg, double E1 )


double Pl_1 (double Ts,double Tr,double Tl, double gamma_s,
double gamma, double Eg, double E1 )


double Pr_1 (double Ts,double Tr,double Tl, double gamma_s,
double gamma, double Eg, double E1 )



//-----------------------------------------//
// P0, Pl and Pr for the upper levels.
//-----------------------------------------//

double P0_2 (double Ts,double Tr,double Tl, double gamma_s,
double gamma, double Eg, double E2 )
```

```
double Pl_2 (double Ts,double Tr,double Tl, double gamma_s,
double gamma, double Eg, double E2 )



double Pr_2 (double Ts,double Tr,double Tl, double gamma_s,
double gamma, double Eg, double E2 )


//-----------------------------------------//
// Transition rates k_dl and k_ld.
//-----------------------------------------//

double k_dl (double Tr, double gamma, double mu, double E){
double rate_dl = gamma*(1-1/(exp((E-mu)/Tr) + 1));
return(rate_dl);
}

double k_ld (double Tr, double gamma, double mu , double E){
double rate_ld = gamma/(exp((E-mu)/Tr) + 1);
return(rate_ld);
}

//-----------------------------------------//
// Main program block.
//-----------------------------------------//


int main()
{
double Tr = 2;
double Tl = 100;
double Ts = 5000;

double gamma_s = 1;
double gamma = 1;
double K_meV = 11.6;
double Eg = 10*K_meV;

int N_e = 1e3;
```

```
int N_t = 1e2;

double E_range = 150;
double T_range = 100;

double dE = E_range/N_e;
double dT = T_range/N_t;

double maxima;

double mu = 0;
double E1,E2,E;

vec  Qr(N_e);
vec Qr1(N_e);
vec Qr2(N_e);
vec Pr1(N_e);
vec Pl1(N_e);
vec P01(N_e);
vec Pr2(N_e);
vec Pl2(N_e);
vec P02(N_e);
vec  J1(N_e);
vec  J2(N_e);

mat Qr_mat(N_e,N_e);

uword max_index;
ofstream output;

output.open("data");

// Qr AS A FUNCTION OF E.

/*
for(int i = 0 ; i < N_e ; i++)
{

E = i*dE;
E1 = - E;
E2 = + E;

Pr1(i) = Pr_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
```

```
Pl1(i) = Pl_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
P01(i) = P0_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);

Pr2(i) = Pr_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
Pl2(i) = Pl_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
P02(i) = P0_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);

J1(i) = Pr1(i)*k_dl(Tr,gamma,mu,E1) - P01(i)*k_ld(Tr,gamma,mu,E1);
J2(i) = Pr2(i)*k_dl(Tr,gamma,mu,E2) - P02(i)*k_ld(Tr,gamma,mu,E2);

Qr1(i) = -(E1 - mu)*J1(i);
Qr2(i) = -(E2 - mu)*J2(i);

Qr(i) = Qr1(i) + Qr2(i);



}

//-----------------------------------------//
// OCCUPATION PROBABILITIES AND Qr AS A FUNCTION OF Tr.
//-----------------------------------------//

dE = 2*K_meV;
Eg = 2*K_meV;

E1 = - dE;
E2 = + dE;


for(int i = 0 ; i < N_t ; i++)
{

Tr = dT*(i+1);

Pr1(i) = Pr_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
Pl1(i) = Pl_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
P01(i) = P0_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);

Pr2(i) = Pr_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
Pl2(i) = Pl_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
P02(i) = P0_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
```

```
J1(i) = Pr1(i)*k_dl(Tr,gamma,mu,E1) - P01(i)*k_ld(Tr,gamma,mu,E1);
J2(i) = Pr2(i)*k_dl(Tr,gamma,mu,E2) - P02(i)*k_ld(Tr,gamma,mu,E2);

Qr1(i) = -(E1 - mu)*J1(i);
Qr2(i) = -(E2 - mu)*J2(i);

Qr(i) = Qr1(i) + Qr2(i);


}



//-----------------------------------------//
SURFACEPLOT OF QR AS A FUNCTION OF E AND Eg.
//-----------------------------------------//

Tr = 50;
Tl = 100;

for(int j=0;j<N_e;j++)
{
for(int k=0;k<N_e;k++)
{

E1 = - dE*(j+1);
E2 = + dE*(j+1);

Eg = dE*(k+1);

Pr1(k) = Pr_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
Pl1(k) = Pl_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
P01(k) = P0_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);

Pr2(k) = Pr_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
Pl2(k) = Pl_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
P02(k) = P0_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);

J1(k) = Pr1(k)*k_dl(Tr,gamma,mu,E1) - P01(k)*k_ld(Tr,gamma,mu,E1);
J2(k) = Pr2(k)*k_dl(Tr,gamma,mu,E2) - P02(k)*k_ld(Tr,gamma,mu,E2);

Qr1(k) = -(E1 - mu)*J1(k);
Qr2(k) = -(E2 - mu)*J2(k);
```

```
Qr_mat(j,k) = Qr1(k) + Qr2(k);

}
}


//-----------------------------------------//
// SURFACE PLOT OF QR AS A FUNCTION OF Tr AND Tl.
//-----------------------------------------//

dE = 2*K_meV;
Eg = 1*K_meV;

E1 = - dE;
E2 = + dE;


for(int j=0;j<N_t;j++)
{
for(int k=0;k<N_t;k++)
{

Tr = (j+1)*dT;
Tl = (k+1)*dT;

Pr1(k) = Pr_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
Pl1(k) = Pl_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
P01(k) = P0_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);

Pr2(k) = Pr_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
Pl2(k) = Pl_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
P02(k) = P0_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);

J1(k) = Pr1(k)*k_dl(Tr,gamma,mu,E1) - P01(k)*k_ld(Tr,gamma,mu,E1);
J2(k) = Pr2(k)*k_dl(Tr,gamma,mu,E2) - P02(k)*k_ld(Tr,gamma,mu,E2);

Qr1(k) = -(E1 - mu)*J1(k);
Qr2(k) = -(E2 - mu)*J2(k);

Qr_mat(j,k) = Qr1(k) + Qr2(k);

}
```

```
}

output << Qr_mat;

//-----------------------------------------//
// DYNAMICAL OPTIMIZATION OF Qr WITH RESPECT TO E AND Eg.
//-----------------------------------------//

for(int t = 1 ; t<= N_t ; t++)
{
Qr.zeros();
maxima = 0;

Tr = dT*t;

for(int i = 0 ; i < N_e ; i++)
{
E1 = - dE*i;
E2 = + dE*i;


Pr1(i) = Pr_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
Pl1(i) = Pl_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);
P01(i) = P0_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1);

Pr2(i) = Pr_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
Pl2(i) = Pl_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);
P02(i) = P0_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2);

J1(i) = Pr1(i)*k_dl(Tr,gamma,mu,E1) - P01(i)*k_ld(Tr,gamma,mu,E1);
J2(i) = Pr2(i)*k_dl(Tr,gamma,mu,E2) - P02(i)*k_ld(Tr,gamma,mu,E2);

Qr1(i) = -(E1 - mu)*J1(i);
Qr2(i) = -(E2 - mu)*J2(i);

Qr(i) = Qr1(i) + Qr2(i);
}

maxima = Qr.max(max_index);

}
}
```

A.2 C++ SOURCE CODE FOR THE DISCRETE MODEL

```
#include <iostream>
#include <math.h>
#include <time.h>
#include <fstream>
#include <iomanip>
#include <armadillo>

using namespace std;
using namespace arma;



//-------------------------------------------------------//
// Quantized energy levels.
//-------------------------------------------------------//

double E1_q (double Delta, double delta, double m){
double discreet_energy1 = -m*Delta - (Delta-delta);
return(discreet_energy1);
}

double E2_q (double Delta, double delta, double n){
double discreet_energy2 = n*Delta + delta;
return(discreet_energy2);
}

//-------------------------------------------------------//
// Transition rates k_dl and k_ld.
//-------------------------------------------------------//

double k_dl (double Tr, double gamma, double mu, double E_dl){
double rate_dl = gamma*(1-1/(exp((E_dl-mu)/Tr)+1));
return(rate_dl);

}
double k_ld (double Tr, double gamma, double mu , double E_ld){
double rate_ld = gamma/(exp((E_ld-mu)/Tr)+1);
return(rate_ld);
}

//-------------------------------------------------------//
```

```
// Main program block.
//-----------------------------------------------------//

int main()
{
double Tr = 2;
double Tl = 100;
double Ts = 5000;

double gamma_s = 1;
double gamma = 1;
double K_meV = 11.6;
double Eg = 10*K_meV;

int N_e = 1e3;
int N_t = 1e2;

double E_range = 1;
double T_range = 1;

double dE = E_range/N_e;
double dT = T_range/N_t;

double Delta = 10;
double delta = Delta*5/10;

double alpha1 = 0.5;
double alpha2 = 0.5;
double beta1 = 0.5;
double beta2 = 0.5;

int    maxima_index;


double mu = 0;
double E1_star,E2_star,E1,E2,E;
double E1_dl,E1_ld,E2_dl,E2_ld;

vec  Qr(N_e);
vec Qr1(N_e);
vec Qr2(N_e);

uword max_index;
```

```
ofstream output;

output.open("data");


cout << " Tl (K) = " << Tl << endl;

cout << " Steplength dE (K) = "<< dE << endl;
cout << " Max energy (K) = "<< E_range << endl << endl;

cout << " Steplength dT (K) = "<< dT << endl;
cout << " Max temperature (K) = "<< T_range << endl << endl;

cout << " Level spacing Delta (K) = "<< Delta << endl;
cout << " Eg (K) = " << Eg << endl;


//-------------------------------------------------------//
// HEAT CAPACITY
//-------------------------------------------------------//

double C_ele;
double Ef = 0*Delta + delta;
vec C_e(N_t);

for(int j=1;j<=N_t;j++)
{
C_ele=0;
for(int i=-5;i<=5;i++)
{
C_ele = C_ele + pow((i*Delta-Ef)/(j*dT),2)*
exp((i*Delta-Ef)/(j*dT))/pow(exp((i*Delta-Ef)/(j*dT))+1,2);
}
C_e(j-1) = C_ele;
output << j*dT << "  " << C_e(j-1)/exp(-(5)/(j*dT))<< endl;
}


//-------------------------------------------------------//
// OPTIMIZATION OF Qr INCLUDING HIGHER ORDER EMISSIONS.
//-------------------------------------------------------//

double Qr1_dl,Qr1_ld,Qr2_dl,Qr2_ld;
```

```
double k_ld_1,k_dl_1,k_ld_2,k_dl_2;
double Qr_temp = 0;
//vec C_e(N_t);
vec maxima(N_t);


// int m_max = int(E_range/Delta);100

for(int t=1;t<=N_t;t++)
{
int m = 0;         // energy level number below the chemical potential
int n = 0;         // energy level number above the chemical potential

maxima_index = 0 ;

Qr.zeros();
Qr1.zeros();
Qr2.zeros();

Tr = dT*t;

for(int i=0; i < N_e ;i++)
{

E = i*dE;
E1 = - E;
E2 = + E;

if( E1 <= - Delta*m - (Delta-delta) )    { m = m+1; }
if( E2 >= + Delta*n + delta )            { n = n+1; }

E1_star = E1_q(Delta,delta,m);
E2_star = E2_q(Delta,delta,n);

for(int j = 0; j<=10  ;j++){

E1_dl = E1_star -     j*Delta;
E1_ld = E1_star + (j+1)*Delta;

k_dl_1 = k_dl(Tr, gamma, mu, E1_dl);
k_ld_1 = k_ld(Tr, gamma, mu, E1_ld);

Qr1_dl = -Pr_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1,E1_ld,E1_dl)*k_dl_1
```

```
*( (E1 - mu)*alpha1 + (E1_dl - mu)*(1 - alpha1) );
Qr1_ld = +P0_1(Ts,Tr,Tl,gamma_s,gamma,Eg,E1,E1_ld,E1_dl)*k_ld_1
*( (E1 - mu)*alpha2 + (E1_ld - mu)*(1 - alpha2) );
double Ef=5;

Qr_temp += Qr1_dl + Qr1_ld;

}

Qr1(i) = Qr_temp;
Qr_temp = 0;

for(int k = 0; k<=10 ;k++){

E2_dl = E2_star - (k+1)*Delta;
E2_ld = E2_star +     k*Delta;

k_dl_2 = k_dl(Tr, gamma, mu, E2_dl);
k_ld_2 = k_ld(Tr, gamma, mu, E2_ld);

Qr2_dl = -Pr_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2,E2_ld,E2_dl)*k_dl_2*( (E2 +
Qr2_ld = +P0_2(Ts,Tr,Tl,gamma_s,gamma,Eg,E2,E2_ld,E2_dl)*k_ld_2*( (E2 +

Qr_temp += Qr2_dl + Qr2_ld;



}

Qr2(i) = Qr_temp;
Qr_temp = 0;

Qr(i) = Qr1(i) + Qr2(i);
}


maxima(t-1) = Qr.max(max_index);

}


}
```

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